ON THE DEVELOPMENT OF AN IDEAL K-VALUE CORRELATION FOR HYDROCARBONS AND ASSOCIATED GASES

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PREFACE

Process conditions being employed in industry today require vapor-liquid K-values at higher pressures, lower temperatures and more varied compositions than was the case a few years ago.

A new correlation method is proposed whereby K-values are found from three terms; namely, (1) an ideal solution K-value, (2) a liquid activity coefficient and (3) a vapor activity coefficient. The work reported in this thesis has concentrated on the development of a correlation for the ideal K-value. Ideal K-values are found from the system pressure, the vapor pressure and the imperfection pressure correction, the latter being obtained from a virial equation of state. The proposed ideal K-value correlation is compared with ideal K-values from three other sources. A brief discussion of liquid and vapor activity coefficients is presented.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Around the turn of the century, when the petroleum industry first became interested in natural gasoline and the 'front end'components of crude oil, it became apparent that the design of processing equipment required some quantitative expression for the composition of a vapor in equilibrium with a liquid. Such an expression was available in a combination of Raoult's and Dalton's laws which state respectively that the partial pressure of any component in a mixture will equal the vapor pressure of that component in the pure state multiplied by its mole fraction in the liquid mixture and that the total pressure, P, of a mixture is equal to the sum of the partial pressures of the components present. Symbolically,

$$y = \frac{p_i^o}{P} x \qquad \text{(I-1)}$$

Defining the equilibrium ratio as

$$K = y/x \qquad \text{(I-2)}$$

then

$$K = \frac{p_i^o}{P} \qquad \text{(I-3)}$$

According to Equation I-3, the equilibrium ratio is equal to the vapor pressure of the pure component at the temperature of the system, divided by the total pressure of the system.

Equation I-3 served industry for many years principally because paraffin hydrocarbons form nearly ideal liquid solutions, thus following Raoult's law, and since processing pressures were low, the deviations from Dalton's law were small.

As markets were developed for propane and butane, the need for process improvements became apparent for the realization of increased propane and butane yields and more economical operations. To accomplish these improvements, higher absorber pressures were required. At the same time, the use of low temperature fractional distillation as an analytical tool was perfected. With these two developments, the flaws in the Raoult's-Dalton's laws became apparent. A new correlation for vapor-liquid equilibrium K-values was necessary.

Fugacity was proposed as a more convenient function for use in making equilibrium calculations. Fugacities, which have the units of pressure, are used instead of chemical potential to express the criteria of equilibria which are

$$T^V = T^L \qquad \text{(I-4)}$$

$$P^V = P^L \qquad \text{(I-5)}$$

$$\bar{f}_i^V = \bar{f}_i^L \qquad \text{(I-6)}$$

where: the subscripts 'i' refer to any component and the superscripts V and L designate vapor and liquid. The bar above f designates the fugacity in a mixture.

In other words: In addition to equal temperature and pressures for each phase the fugacities of each component must be the same in both phases. This fugacity criteria is equivalent

to equal chemical potential for each component in both phases.

Instead of Raoult's law, ideal solutions may be assumed by replacing the pressures in Equation I-1 by fugacities

$$xf^L = yf^V \qquad \text{(I-7)}$$

where: f^L = fugacity of the pure component as liquid at the equilibrium temperature and pressure

f^V = fugacity of the pure component as vapor at the equilibrium temperature and pressure

Ideal equilibrium ratios were devised based on

$$K = \frac{y}{x} = \frac{f^L}{f^V} \qquad \text{(I-8)}$$

It was found that fugacities could be extrapolated into regions above the critical temperature. Thus the developmemts of the correlations reviewed in Chapter II had their beginning.

New K-Value Correlation Form

Vapor-liquid K-values of hydrocarbons and similar substances are known to be functions of vapor pressure and the total pressure on the system, at least. In the pure state the vapor and total pressures are sufficient to define the phase condition. For an ideal mixture of components whose vapor phase obeys the perfect gas law the vapor and total pressures lead to the K-values used in computing the composition of the coexisting liquid and vapor phases.

Departure from perfect gas laws due to high pressures or low temperatures and from ideal solutions due to non-additivity of both vapor and liquid volumes can best be handled by separate parts of the correlations. A correlation of this type should be

more general and meaningful to the design engineer than one in which these departures from ideal solution and perfect gases are combined as in a computer program based on an equation of state.

The K-value correlation that meets the above requirements is the following:

$$K_{Actual} = K_{Ideal} \frac{\gamma_i^L}{\gamma_i^V} \qquad (I-9)$$

As noted by the subscript, the K-values apply to the 'actual' system and an 'ideal' system in which the equilibrium vapor and liquid mixtures are ideal, i.e., volumes are additive.

The activity coefficients, γ_i^L and γ_i^V, are numerical measures of the departure of the liquid and vapor phases from ideal solutions. These activity coefficients are functions of the compositions of the equilibrium phases for each component of the system and represent all effects of composition on the K-value.

Only one of the four terms in Equation I-9 can be measured experimentally, namely, K_{Actual} which is equal to y/x. If two of the remaining three terms can be calculated by theoretical equations or estimated by empirical methods, the remaining term can be 'back-calculated'. This is the procedure that is being used in this work.

The procedure in the overall correlation development is to develop an ideal K-value correlation and then to use this along with the experimental K-ratios available in the literature and the Scatchard-Hildebrand (76) liquid activity coefficients to derive the vapor activity coefficients. A generalized activity

coefficient will complete the correlation.

Previous work (15,65) has shown that the Scatchard-Hildebrand 'regular solution' equation is a satisfactory relationship for predicting the liquid phase activity coefficients for the components of hydrocarbons and gases. Although this 'regular solution' equation has limitations, e.g., it always yields activity coefficients that are greater than unity; it is satisfactory for most hydrocarbon systems.

Values of K_{Ideal} are required to obtain vapor activity coefficients. The ideal K-value is the ratio of pure component fugacities (i.e., f_i^L/f_i^V) and appears to be susceptible to theoretical thermodynamic calculations. For any mixture in a vapor-liquid phase equilibrium state either f_i^L or f_i^V, but not both, may be computed from PVT data. This limitation is due to the fact that one pure state (liquid or vapor) will always be hypothetical for all components of a mixture. This situation has been confronted by everyone that has attempted to develop generalized and comprehensive K-value correlations. Different techniques have been used to try to circumvent the problems caused by the hypothetical states.

The hypothetical states arise when one of two situations exists for a mixture. First, a component in the gas phase may be present at a pressure exceeding its vapor pressure, thus the vapor state for the pure component is hypothetical. Second, a component in the liquid phase may be present at a temperature exceeding its critical temperature, thus the pure component liquid is hypothetical. Edmister (18) and Prausnitz (66) have discussed hypothet-

ical states in considerable detail in recent papers.

Purpose of This Work

The purpose of this work is to develop generalized ideal K-values that are suitable for the overall K-value correlation scheme.

A new procedure has been used in this work to develop generalized ideal K-values that are suitable for the correlation plan of this K-value development. As will be shown the new correlation for ideal K-values is of the form

$$K_{Ideal} = K^{o} \, (K')^{\omega} \qquad \text{(I-10)}$$

$$\ln K_{Ideal} = \ln K^{o} + \omega(\ln K') \qquad \text{(I-11)}$$

where: K^{o} and K' are functions of P_r and T_r only

ω = acentric factor

In Equations I-10 and I-11, K^{o} is the ideal K-value for a simple fluid for which $\omega = 0$ and K' is a measure of the departure from a simple fluid. The use of the acentric factor as one parameter in correlating the ideal K-values was suggested by the PVT and vapor pressure correlations developed by Pitzer and Curl (64).

From actual and ideal K-values and the liquid activity coefficient the vapor activity coefficient may be found by back calculations as shown in the following relationships

$$\gamma^{V} = \frac{K_{Ideal}}{y/x} \gamma^{L} \qquad \text{(I-12)}$$

$$\ln \gamma^{V} = \ln K_{Ideal} - \ln y/x - \ln \gamma^{L} \qquad \text{(I-13)}$$

The logarithmic forms of Equations I-11 and I-13 are included to show the forms used in the development calculations.

Three different correlation schemes for K_{Ideal} were developed and subsequently tested

1. A correlation based on modified f/P values
2. A correlation based on x-y data and equation of state calculations.
3. A correlation which uses vapor pressures and virial coefficients through the imperfection pressure correction.

CHAPTER II

HIGHLIGHTS IN THE DEVELOPMENT OF VAPOR LIQUID EQUILIBRIUM CORRELATIONS

The fugacity of a component in a mixture of gases is related to composition and to the variables of state by the rigorous thermodynamic relationship (17)

$$RT \ln \frac{\bar{f}_i}{f_i x_i} = \int_o^P (\bar{V}_i - V_i)\, dp \qquad \text{(II-1)}$$

The subscript "i" refers to any component. The bar above f designates the value of the fugacity in a mixture.

Equation II-1 is applicable to both liquid and vapor phases. It is written here for the liquid; thus the composition of component i is denoted as x_i. For the vapor phase, x_i would be replaced by the vapor mole fraction, y_i.

The above equation makes use of fugacity, a quantity devised and proposed by G. N. Lewis (47) in 1901 as a function more convenient for making equilibrium calculations than chemical potential.

Lewis defined fugacity in terms of the free energy

$$dG = (RT\ d \ln f)_T \qquad \text{(II-2)}$$

subject to the requirement that

$$\lim_{P \to 0} \left(\frac{f}{P}\right) = 1.0 \qquad \text{(II-3)}$$

For a thorough discussion of fugacity refer to the work of Tunell (84).

Rigorous thermodynamic relations almost always require more experimental data than are available, therefore, empirical rules or simplifying assumptions become necessary. Such is the case with Equation II-1.

Often the partial volumes, $\bar{V}_i$, are not available. Furthermore, the pure component molar volume, V_i, may be hypothetical. To circumvent these difficulties, Lewis and Randall (47) introduced the assumption of additive volumes (Amagat's Law), i.e.,

$$\bar{V}_i^{\,V} = V_i \qquad \text{(II-4)}$$

Using Equation II-4, Equation II-1 reduces to the expression known as the Lewis and Randall rule

$$\bar{f}_i = x_i f_i \qquad \text{(II-5)}$$

The additive volume assumption can be a drastic one especially for the liquid phase. Gilliland and Sullivan (27) have pointed out that the Lewis and Randall rule can give large errors at high pressures. As a criterion for most mixtures, it is not likely to be satisfactory at pressures much greater than 0.6 times the critical pressure of the component in question.

The first great strides toward predicting hydrocarbon vapor-liquid equilibria were made in the period 1930 to 1940. Generalized fugacity correlations were prepared by making use of available compressibility data, the Lewis and Randall rule and the assumption of van der Waals' law of corresponding states. Two significant equilibrium constant correlations resulted from

these generalized fugacity correlations: (1) The MIT K-charts of W. K. Lewis (52) and (2) The Michigan K-charts of G.G. Brown (12).

MIT K Charts

Lewis and Kay (53) and Newton (58) developed correlations whereby the ratio of the fugacity to the pressure, f/P, was shown to be determined substantially by the reduced pressure, P_r, and the reduced temperature, T_r. These correlations were based primarily on PVT data available for pure hydrocarbons. The f/P values for the lower reduced temperatures were obtained by extrapolation of the PVT data and by using equilibrium data for several binary systems.

Charts of vapor-liquid equilibrium K-values for hydrocarbons were prepared from f/P vs. T_r and P_r correlations and some experimental data on the solubility of light gases.

The MIT K-values prepared in the early 1930's were derived through cognizance of equal chemical potential between phases, assumption of the Lewis and Randall rule for both phases and neglect of the influence of pressure on the liquid fugacity.

These correlations did not take into account the composition of the system and the influence of the chemical nature of the constituents. Such inadequacies in these two correlations were recognized early. Except for the use of experimental data, these correlations did little more than correct for the non-ideal behavior of the gas phase.

The MIT K-charts do not give completely ideal K-values, even though temperature and pressure are the only variables. An example of the use of these charts may be found in Chapter 18 of Edmister's book, Applied Hydrocarbon Thermodynamics.

The Michigan K-value charts (12) were developed in a manner similar to that of the MIT charts and need not be discussed also.

Polyco K Charts

The Polyco[1] work was done by Benedict, et al. at M. W. Kellogg's Jersey City Laboratory. The fugacities of 12 light hydrocarbons were calculated using the Benedict equation of state (7).

The authors found that the effect of composition on fugacity and the K-values could be represented with sufficient accuracy by a single composition variable for each phase, the molal average boiling point for mixtures and conditions studied by them. This was admitted to be a compromise between precision and practicality, but the results otherwise would have been unwieldy. With this simplification fugacity calculations were made for selected binary hydrocarbon systems in such a way as to simulate all possible mixtures of the seven normal paraffins between methane and n-heptane. By selecting binary systems, the assumption was made that the balance of the mixture could be treated as a single average hypothetical component. This is an approximation which has

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[1]Polymerization Process Corporation, a polymerization patent holding company jointly owned by Texaco, Pure, Phillips, Standard Oil (Indiana) and Kellogg.

been justified by the results. The resulting binary system fugacity coefficients were correlated as a function of pressure, temperature and the molal average boiling point of the phase in question.

The original charts were plots of fugacity coefficients against temperature. These were replotted and published by the M. W. Kellogg Company in 1950 (45). Publication was in two parts, one containing 144 charts of K-values with correction factors for pressures up to 1000 psi and the other containing 132 charts of fugacity coefficients for pressures from 1000 to 3600 psi.

De Priester (16) using additional experimental K data, modified the atmospheric to 1000 psi Kellogg charts to the form of two parameter charts, one for the liquid phase and one for the vapor phase for each hydrocarbon, thus condensing 144 charts to 24 charts and at the same time improving the accuracy of the correlation.

Edmister-Ruby Correlation

Using the fugacity values obtained by Benedict et al. (7,9), Edmister and Ruby (21) developed generalized correlations giving vapor and liquid activity coefficients as functions of reduced temperature, reduced pressure and boiling point ratio. The correlation of Benedict et al. was reduced from 276 charts to six charts which can be used directly in reduced units to obtain equilibrium vapor-liquid distribution ratios, or to prepare K-value plots for individual hydrocarbons with specific temperature and pressure scales.

These correlations are completely generalized and contain none of the original adjustments used by De Priester in his improvement of the Polyco charts. Edmister and Ruby (21) present statistical evidence that their correlation is as good as that of De Priester and it may be better due to the generalization included.

Watson et al. Charts

This K-value correlation had its beginning at the University of Wisconsin and was completed at the Sinclair Refining Company.

Gamson and Watson (27) proposed that the phenomenon of the convergence of equilibrium ratios of components of mixtures to K = 1.0 be taken into account by means of activity coefficients to express the deviation from ideal solution behavior in the liquid and vapor phases.

On the basis of generalized fugacity coefficients and the pseudo critical concept, Gamson and Watson developed equations for the activity coefficients. These equations were simplified and modified empirically by Smith and Watson (80) as a basis for a general graphical correlation of activity coefficients, as functions of the pseudocritical temperatures and pressures of the phases. The resulting charts were published by Smith and Smith (81).

The Smith and Watson activity coefficients and the dependent Smith and Smith charts suffer from two limitations: (1) The simplified critical ratio assumption for temperature and pressure made in the vapor phase correlation which is valid for paraffin

hydrocarbons only and (2) the use of pseudo reduced conditions in developing the liquid phase activity coefficient correlation.

Prausnitz-Edmister-Chao Correlation

Prausnitz-Edmister-Chao (65) developed a method for correlating vapor-liquid K-values for conditions where deviation from ideal solutions arises mainly in the liquid phase.

The K-value for component "i" is computed by the rigorous thermodynamic relation

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i \nu_i}{\phi_i} \qquad \text{(II-6)}$$

$$\gamma_i^L = \frac{\bar{f}_i^L}{f_i^L x_i} = \text{the liquid phase activity coefficient for component "i"}$$

$$\phi_i^V = \frac{\bar{f}_i^V}{P y_i} = \text{the vapor phase fugacity coefficient for component "i"}$$

$$\nu_i = \frac{f_i^L}{P} = \text{the liquid phase fugacity coefficient for pure component "i"}$$

The three coefficients, γ_i, ν_i and ϕ_i are evaluated at system conditions, i.e., the temperature and pressure of the system. The reference state for the liquid activity coefficient is the same pure component fugacity that appears in the ν_i term, thus making the numerator terms, γ_i and ν_i compatible.

The Redlich-Kwong (68) equation of state was used by these authors for evaluating ϕ_i and the Scatchard-Hildebrand relationship (76) was used for evaluating γ_i. The solubility parameters,

liquid volumes and pure liquid fugacity coefficients for light gaseous solutes were derived from experimental vapor-liquid equilibria data and these relationships.

The liquid activity coefficient, γ_i, is a measure of the departure from ideal solutions. The vapor fugacity coefficient, ϕ_i, is a measure of the combined departure from perfect gases and from ideal vapor mixtures. Thus the nonideality terms in the PEC equation are measures of different departures for the liquid and vapor mixtures.

The work of Prausnitz, Edmister and Chao demonstrated the following:

(1) The calculation of light hydrocarbon vapor-liquid equilibria by the use of solubility parameters appears to give correctly the liquid phase composition effects. The solubility parameter is a useful tool for the correlation and prediction of hydrocarbon vapor-liquid equilibria.

(2) Composition-corrected K-values are not convenient to apply in practical problems and this method is no exception.

(3) Simplification can be obtained by taking the solubility parameter to be pressure insensitive.

Pigg (60) in a study of ethane binaries used the method suggested by Prausnitz, Edmister and Chao with the added simplification that the solubility parameter was assumed to be insensitive to temperature as well as pressure. The average predicted K-values were reported to deviate only 6 per cent from exper-

imental values, compared to 26 per cent when using the NGAA convergence pressure method (57). A similar study was made by Pipkin (61) for methane binaries.

Chao-Seader Correlation

Chao and Seader (15) developed a general correlation for vapor-liquid equilibria using the equation used by Prausnitz, Edmister and Chao (65) in their work (Equation II-6).

The pure liquid fugacity coefficient, ν_i, is primarily responsible for reflecting the effects of component identity, temperature and pressure. It is analagous to the familiar 'ideal' K-value. It is identical to the true K-value when the vapor mixture is an ideal gas and the liquid solution is also ideal, i.e., $\phi_i = 1.0$ and $\gamma_i = 1.0$.

The fugacity coefficient in the vapor mixture, ϕ_i, is always close to unity at sufficiently low pressures. As pressure is increased, it decreases markedly for the heavy components, however, for the light components, it usually changes only slightly.

The activity coefficient in the liquid solution, γ_i, approaches unity for the component present in high concentration in the liquid phase. It takes the place of the 'aromaticity correction factor' in common use for light components (83).

The fugacity coefficient, ν_i, is a pure component property; it may be correlated in the framework of the principle of corresponding states. The activity coefficient, γ, is usually ex-

pressed in terms of either van-Laar or Margules type of equations. Hildebrand's equation (76), which is of the van-Laar type was used by Chao and Seader in their work. The relatively simple Redlich-Kwong equation (68) has been found to yield satisfactory results over a wide range of conditions for calculation of ϕ.

This K-value correlation applies to hydrocarbons of various types, including paraffins, olefins, aromatics and naphthenes. The final correlation has been tested by the authors on mixtures of the above types of compounds. The overall average deviation from 2700 experimental data points was reported by Chao and Seader to be 8.7%.

The Chao-Seader K-value correlation has been programmed for the IBM 650 digital computer by Edmister, Joyner and Maddox (22). The equations in the Chao-Seader correlation can be solved to get the vapor-liquid K-values for a mixture providing the compositions of the coexisting equilibrium vapor and liquid phases are known (given, assumed or from a previous trial). In applying this K-value prediction method, it is necessary to check bubble point, dew point or flash calculations to see if the resulting compositions agree with those used in the K-value predictions.

Two forms of the Chao-Seader IBM 650 computer program are available. The first uses the augmented 650 with automatic floating decimal, indexing registers and immediate access storage. Three options are included in this program: a bubble point calculation, a dew point calculation and a flash calculation.

The second program uses only the automatic floating decimal and indexing registers. Two options are included in this deck:

a bubble point calculation and a dew point calculation. The flash calculation was omitted since this calculation is excessively time consuming without immediate access storage.

Chao and Seader developed their K-value correlation using the IBM 704 digital computer. Chao and Seader have prepared a computer program for this machine.

Convergence Pressure-Based Correlation

The understanding of the idea of convergence pressure is facilitated by considering a pressure-equilibrium plot for a binary mixture at constant temperature (Figure 1). When the K-values for both components are plotted in this way, the resulting curve crosses K = 1.0 at two points, namely, the vapor pressure of the heavier component and the convergence pressure of the mixture.

The convergence pressure of a hydrocarbon system for a given temperature is the pressure at which the K-values of all components of the system are equal to unity. The convergence pressure of a binary is the critical pressure of the mixture of the binary components that has a critical temperature equal to the system temperature.

The latter definition of convergence pressure works fine so long as the system temperature is between the critical temperature of the two components. For a binary system the convergence pressure is set by the system temperature and identity only. For a multicomponent system the convergence pressure is a function of composition also. The major disadvantage of the convergence pres-

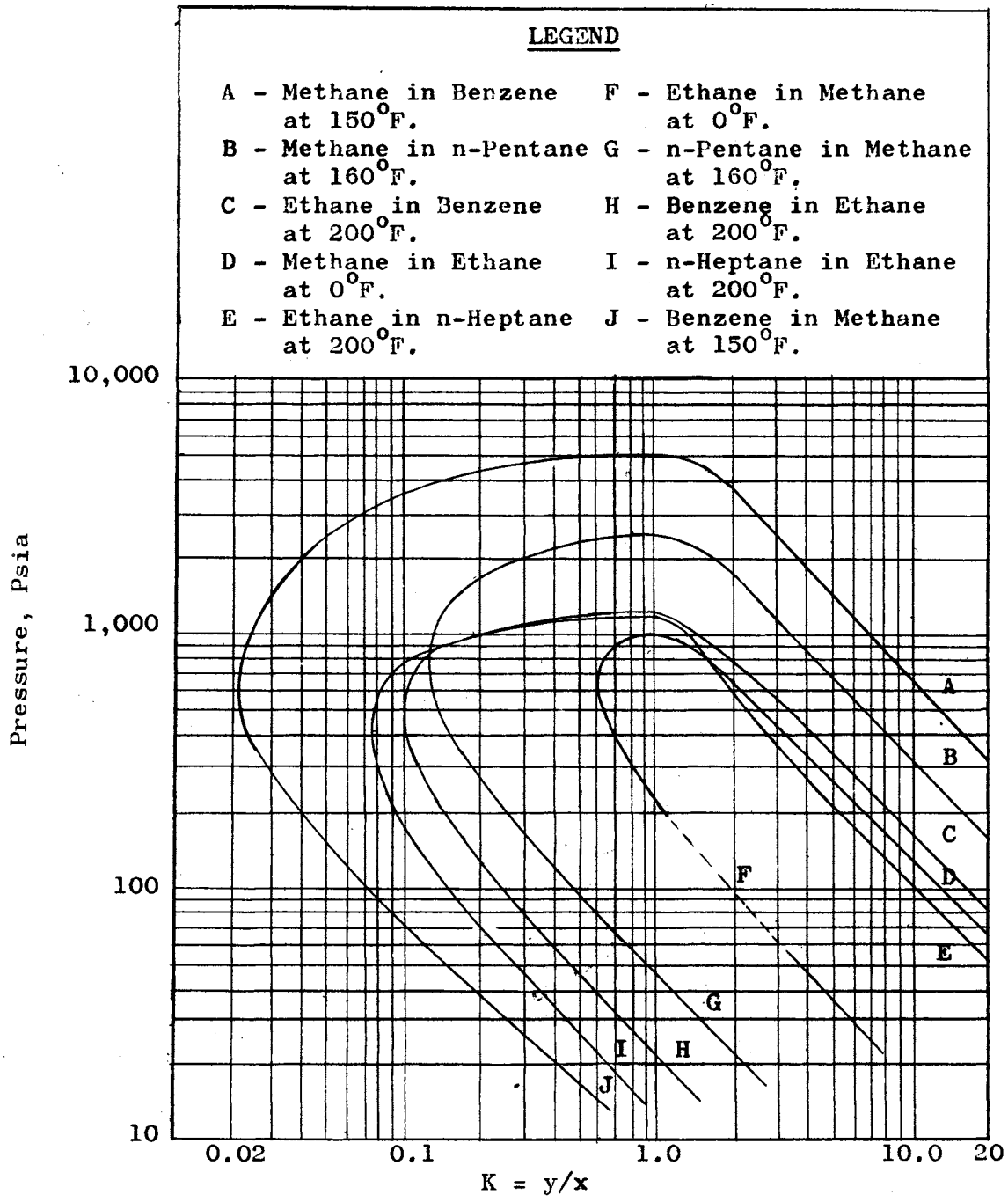

Figure 1

Convergence Pressure Concept for Vapor-Liquid K Correlations (20)

sure as a correlating parameter is that there is no theoretical method for calculating the convergence pressure of a multicomponent system. In fact, there is not even a generally accepted definition of convergence pressure for a multicomponent system.

Hadden (33) developed a theory of convergence pressure for ternary and more complex systems which was shown to be commensurate with Gibbs' phase rule. Hadden showed the convergence pressure to be a function of the operating temperature and of the liquid-phase composition exclusive of the lightest component concentration. Hadden introduced the concept of quasi-convergence pressure for temperatures below the critical temperature of the lightest component.

The quasi-convergence pressure has no physical significance. It is merely a convenient correlating parameter. All of the evidence to date indicates that the quasi-convergence pressure is a function of the light component identity alone and is independent of the heavy component identity. For binary mixtures the quasi-convergence pressure can be taken as the critical pressure of the lightest component.

None of the convergence pressure methods are based on theoretical developments as are the K-value correlation methods discussed earlier. Each of the different convergence pressure methods attempts to correlate empirically the bulk of vapor-liquid equilibria data available in the literature.

In 1933, Katz and Brown (40) pointed out that in order to predict the K-value of any component at a given temperature and

pressure one must know the molecular weight, critical temperature and vapor pressure of the component and the critical point of the mixture. These authors further stated that the K-value is unity for a component when its vapor pressure equals the system pressure and that the K-value is also unity at the critical point of the mixture. These authors did not define the convergence pressure, but they did state the fundamental principles of it.

Katz and Hachmuth (41) in 1937 investigated the variation of hydrocarbon-natural gas-crude oil K-values with pressure by making actual phase equilibria measurements. These pressure effects were shown on log K vs. log P scales with one chart for each temperature. The point of interest was that for each hydrocarbon, all curves intersected the unity K-value at a pressure above the pressure of the highest measurement.

White and Brown (89), investigating narrow petroleum cuts in 1942, showed the convergence pressure phenomenon for hydrocarbons from pentane up to the 725°F. boiling point. They also presented critical locus curves for a naphtha and for a furnace oil. Using their own data and data previously published these authors correlated the minimum K-value for the higher boiling components with vapor pressure and with convergence pressure.

Rzasa et al. (72) developed a correlation for predicting the convergence pressure of systems containing methane or natural gas with complex hydrocarbon mixtures ranging from natural gasoline to crude oils. The resulting correlation gave convergence pressure as a function of the temperature and the product of

molecular weight and specific gravity of the heptane plus fraction.

Organick and Brown (59) developed an empirical correlation of the convergence pressure type for equilibrium volatility ratios. In this correlation the convergence pressure is found from the molal average boiling point of the equilibrium phase and the average molecular weight of the equilibrium liquid. This method involves trial and error which is an obvious disadvantage.

There are two K-value correlations that use the nomographic technique. These are the Winn (90,91) correlation and the Braun correlation described by Lenoir et al. (46,47,48,49).

The Winn correlation is applicable to light hydrocarbons, narrow cut petroleum fractions and certain non-hydrocarbons. The Winn nomographs are presented as a function of the system temperature and pressure and the composition of the liquid phase. The composition is taken into account by use of a convergence pressure parameter and a solvent-character parameter.

The Winn correlation consists of a basic nomogram applicable from 40 to 800°F. and 10 to 5000 psia to systems of paraffin hydrocarbons from methane through heptane, to the olefins of the corresponding boiling point and to certain non-hydrocarbons.This nomogram is for a constant convergence pressure of 5000 psia. The basic nomogram can be corrected to system pressures up to 10,000 psia by use of a correction plot. A second coordinate plot and an equation are provided to obtain K-values for high-boiling compounds and narrow-cut petroleum fractions. The coordinate plot and the equation are used in conjunction with the

basic nomograph. Winn suggests that the Hadden correlations and methods for evaluating the convergence pressure be used in conjunction with his correlation.

The Braun K-ratio correlation is based upon the use of an intermediate parameter, K_{10}, which is the K-value at the system temperature and 10 psia for the hydrocarbon in question. By means of this intermediate parameter the variables affecting the K-value have been factored out so that K_{10} is a function of temperature and the component while the actual K-value is a function of K_{10}, pressure and the convergence pressure.

In using the Braun (36) correlation to obtain an equilibrium ratio, there are three steps. First we compute the convergence pressure, or the quasi- convergence pressure, of the multicomponent hydrocarbon mixture. Second, we look up the low pressure equilibrium value, the K_{10}, for each component of the mixture. Third, we find the equilibrium ratio at the system pressure for each component.

The Braun correlation is applicable to 68 aliphatic, olefinic, aromatic and naphthenic hydrocarbons. The correlation is also applicable to hydrocarbon systems containing small amounts of hydrogen, carbon monoxide, nitrogen, hydrogen sulfide and water. The temperature range is -200 to 900°F. and the pressure range is 10 to 10,000 psia. All components are not covered over the above mentioned temperature and pressure ranges.

The NGAA K-charts (57) published in 1955 were constructed by the Fluor Corporation from data compiled by Dr. G.G. Brown and by Fluor. The decision was later made to expand the data into lower

temperature ranges than those previously covered. This was done by extrapolation and cross plotting. Equations have been fitted to these K-charts and a digital computer program has been developed for calculating K-values from temperature, pressure and convergence pressure. The NGAA K-charts are widely used and have served industry reasonably well for calculating equilibrium ratios for a wide range of hydrocarbon mixtures.

These charts are based on a convergence pressure derived from a hypothetical binary liquid. This pseudo-binary mixture is composed of the lightest component of the mixture and a hypothetical heavy component. The hypothetical heavy component is composed of all components other than the lightest component. One uses a weighted average method to obtain the critical temperature and pressure of this 'heavy component'. Generally, only the use of the critical temperature of the 'heavy component' is necessary to draw a critical loci curve from which the convergence pressure can be read. After the convergence pressure is determined, the K-values are read from charts for the nearest convergence pressure.

The charts for the lower convergence pressures are based largely on data from the binary paraffin systems investigated by Sage, Lacey and co-workers. The higher convergence pressure charts are based on data for mixtures of lower molecular weight hydrocarbons with complex mixtures of higher molecular weight hydrocarbons. The higher molecular weight mixtures contained non-hydrocarbon species and data from these mixtures are not consistent with data on mixtures containing normal paraffins. Other inconsistencies were introduced with the extrapolation and cross plot-

ting used to expand the correlation.

CHAPTER III

IDEAL K-VALUES FROM MODIFIED GENERALIZED f/P CORRELATIONS

The basic K-value expression for this correlating scheme can be obtained from the correlation equation of Prausnitz, Edmister and Chao (65) and that of Chao and Seader (15)

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i \nu_i}{\phi_i} \qquad \text{(III-1)}$$

By multiplying and dividing Equation III-1 by $(f/P)_i$, the fugacity coefficient of the component in the pure vapor state

$$K_i = \frac{\gamma_i}{\left(\frac{\phi}{f/P}\right)_i} \left(\frac{\nu}{f/P}\right)_i \qquad \text{(III-2)}$$

$$= \frac{\gamma_i^L}{\gamma_i^V} K_{Ideal} \qquad \text{(III-2a)}$$

where:

$$\gamma_i^V = \left(\frac{\phi}{f/P}\right)_i = \left(\frac{\bar{f}}{yf}\right)_i^V$$

$$K_{Ideal} = \left(\frac{\nu}{f/P}\right)_i = \frac{f_i^L}{f_i^V}$$

$$\gamma_i^L = \left(\frac{\bar{f}}{xf}\right)_i^L$$

The activity coefficients, γ^L and γ^V, in Equation III-2 represent the departures from ideal mixtures in the liquid and vapor phases, respectively. For the heavier 'solvent' components of a mixture, the values of γ^L will be nearer unity than the γ^L for the lighter 'solute' components of the mixture. Similarly, the values of γ^V will be nearer unity for the lighter 'solute' components than for the heavier 'solvent' components. Both γ^L and γ^V approach unity as the concentrations approach unity, i.e., γ^V approaches unity as the vapor phase concentration approaches unity and γ^L approaches unity as the liquid phase concentration of the solvent approaches unity.

Because of these effects and trends, it appears logical to express the K-value as a function of γ^L, γ^V and K_{Ideal} as shown in Equation III-2. K_{Ideal} is visualized as a function of temperature and pressure only for each component while the activity coefficients, γ^L and γ^V, are functions of the physical properties of the mixture components, concentrations and conditions.

This K_{Ideal} correlation was developed from the Pitzer (51) and Prausnitz (66) generalized f/P correlations for pure and hypothetical vapors and the Chao and Seader (15) correlation for real and hypothetical liquids. This was based on the following combination of equations

$$K_{Ideal} = \frac{\nu}{f/P} \qquad \text{(III-3)}$$

$$K_{Ideal} = \frac{\nu^o}{(f/P)^o} \left(\frac{\nu'}{(f/P)'} \right)^{\omega} \qquad \text{(III-4)}$$

$$K_{Ideal} = K^{o} (K')^{\omega} \qquad \text{(III-5)}$$

where: K^{o} = Ideal K-value for the simple (=0) fluid
K' = Correction for departure from the simple fluid
$\nu = (f/P)_{L}$

Chao and Seader (15) developed empirical correlations for ν^{o} and ν'. Pitzer, et al. (62,63,64) developed correlations for $(f/P)^{o}$ and $(f/P)'$ in the real gas region. Prausnitz (66) extended the f/P correlations into the hypothetical vapor state and Edmister (19) put this hypothetical f/P correlation into $(f/P)^{o}$ and $(f/P)'$ form.

Changes were made in the Prausnitz (66) hypothetical vapor, $(f/P)^{o}_{V}$, and in the Chao and Seader (15) hypothetical liquid, ν^{o}_{L}, values to satisfy the requirement that $K^{o} = 1.0$ at the vapor pressure. These revisions were made for each reduced temperature. The method of revision is illustrated in Figure 2 for $T_{r} = 0.8$ and in Figure 3 for $T_{r} = 1.4$.

At reduced temperatures less than unity the $(f/P)^{o}_{V}$ curves for the hypothetical vapor were revised to intersect the ν^{o}_{L} curves at the vapor pressure, assuming the correctness of the ν^{o}_{L} curves at $T_{r} < 1.0$. Similarly, the curves were revised for reduced temperatures greater than unity to intersect the $(f/P)^{o}_{V}$ curves at the vapor pressure (extrapolated), thus accepting the $(f/P)^{o}_{V}$ values for the real vapor. These modifications can be only made at the vapor pressures, which is an obvious limitation.

Using these revisions in the hypothetical vapor and liquid fugacity coefficients, revised plots were made of ν^{o} and $(f/P)^{o}_{V}$ as functions of reduced temperature and reduced pressure. Figure 4 is a composite of the $(f/P)^{o}_{V}$ values of Pitzer et al. (51) at

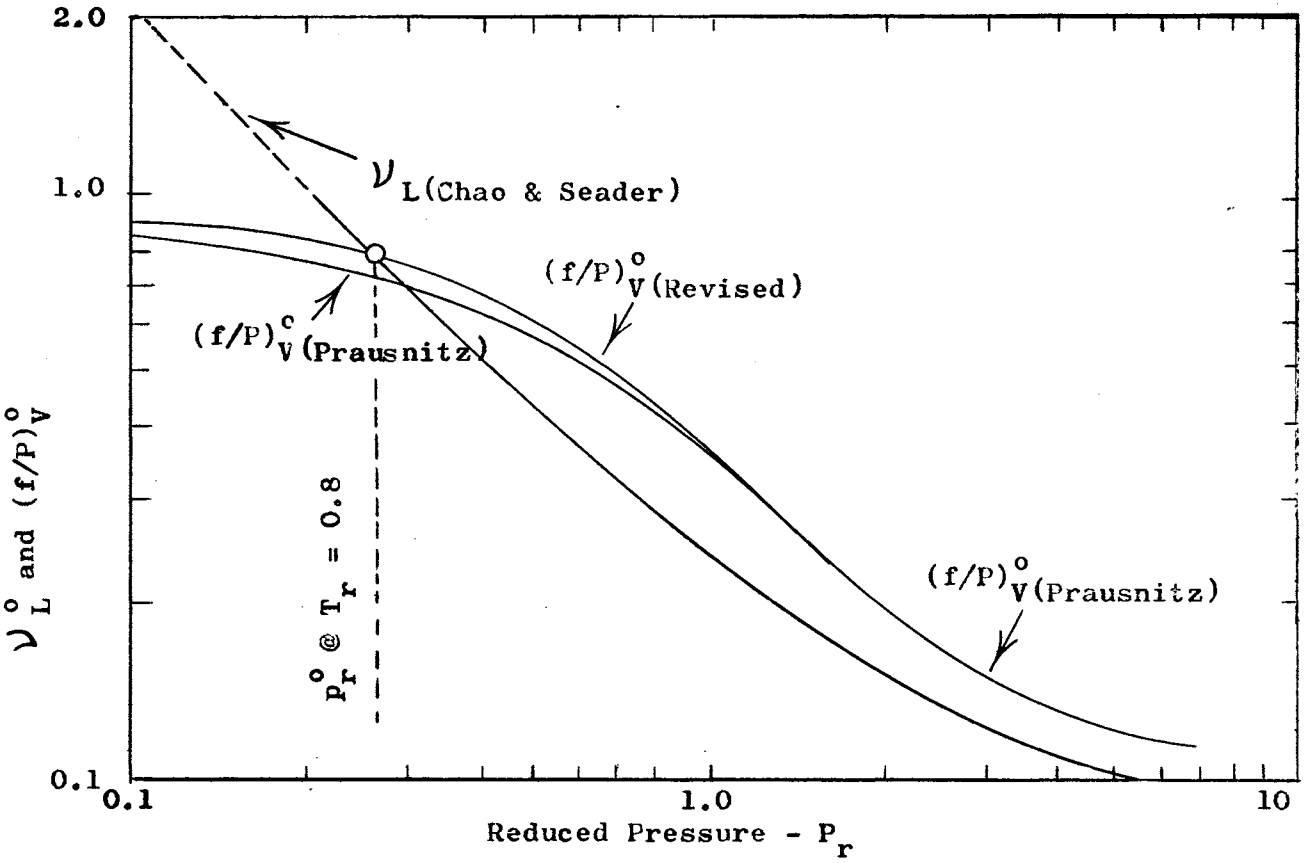

Figure 2

Illustration of Adjustment of Vapor Fugacity Coefficient at the Vapor Pressure, T_r = 0.8 (24)

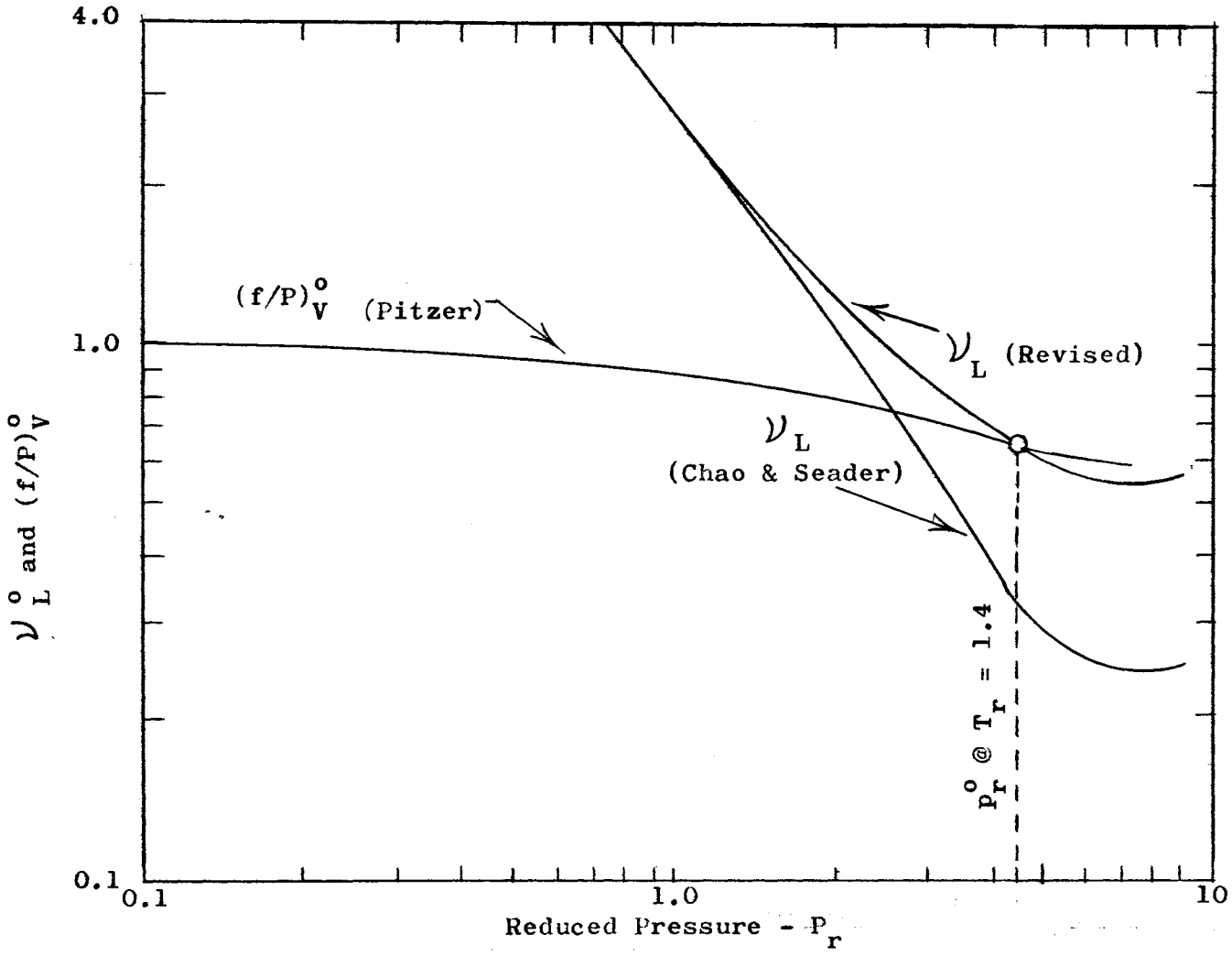

Figure 3

Illustration of Adjustment of Vapor Fugacity Coefficient at the Vapor Pressure, T_r = 1.4 (24)

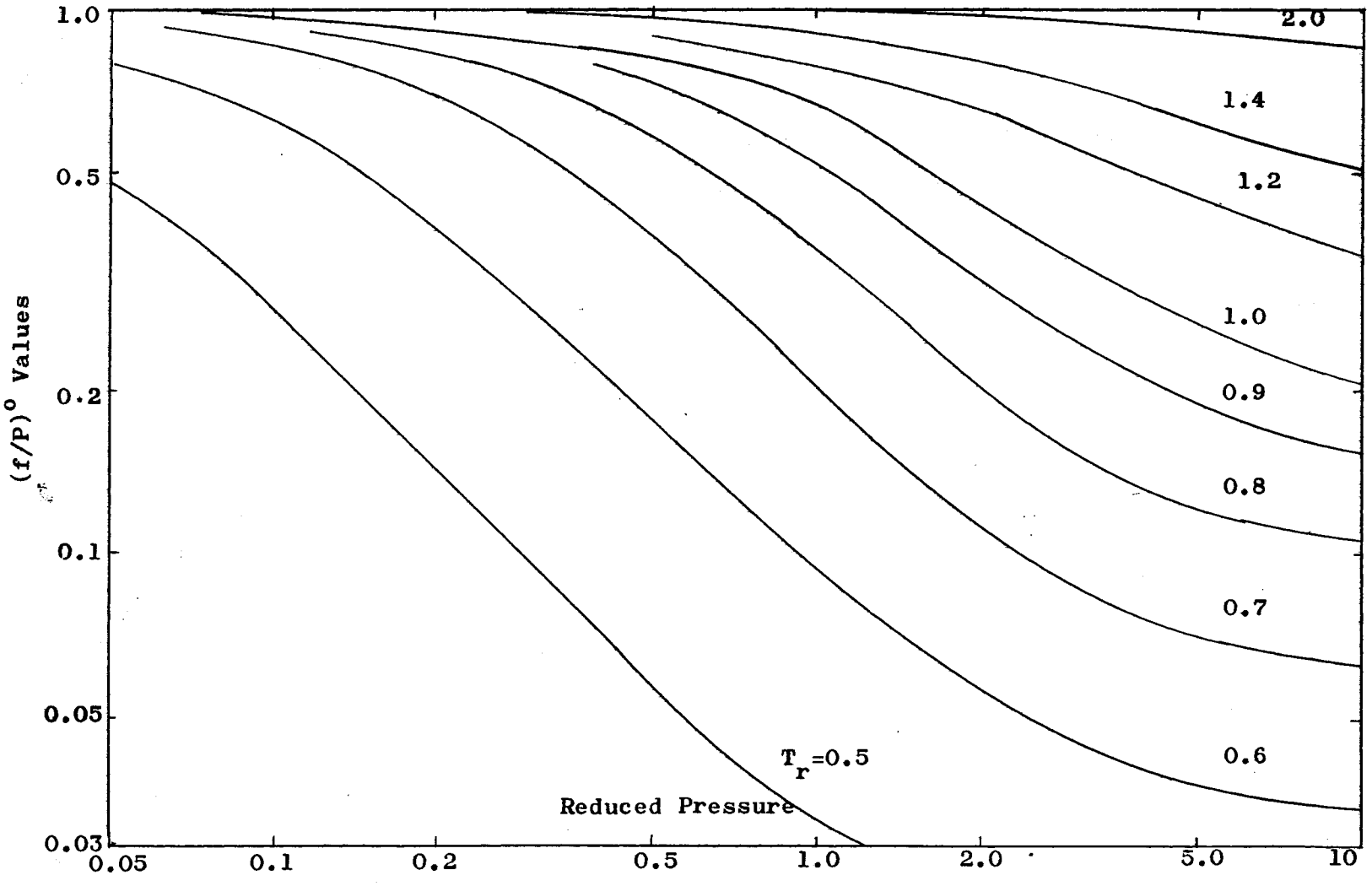

Figure 4

Smoothed Values of Fugacity Coefficient for Pure Simple Vapor (24)

reduced temperatures equal to and greater than unity and the modified hypothetical vapor state $(f/P)_V^o$ values of Prausnitz (66) for reduced temperatures less than unity. Two bases were used in making the revisions to the curves for the low reduced temperatures: (1) the vapor pressure intersection criterion of Figures 2 and 3 and (2) reasonable and smooth cross plots of K_{Ideal}^o as a function of reduced temperature and reduced pressure. No revisions were made to the $T_r \geq 1.0$ isotherms of Pitzer, et al.

A simple fluid liquid fugacity coefficient plot, Figure 5, was prepared from the ν_L^o values of Chao and Seader after making the following revisions: (1) The $T_r > 1.0$ isotherms were raised in the higher pressure region by the vapor pressure intersection requirement of Figures 2 and 3 and (2) The higher pressure end of the $T_r < 1.0$ isotherms were raised by cross plotting to give smooth curves that yielded K_{Ideal} values which conformed to known trends.

Ideal K-values for the simple fluid were calculated using the smoothed, pure component fugacity coefficients from Figures 4 and 5. These K-values are shown in Figure 6 as a function of reduced temperature and reduced pressure.

There are two ways of evaluating the correction term, K': (1) directly from the correction terms of the generalized f/P correlations described above and (2) from the requirement that $K_{Ideal} = 1.0$ at the vapor pressure for substances of different acentric factor.

In terms of the fugacity / pressure ratio

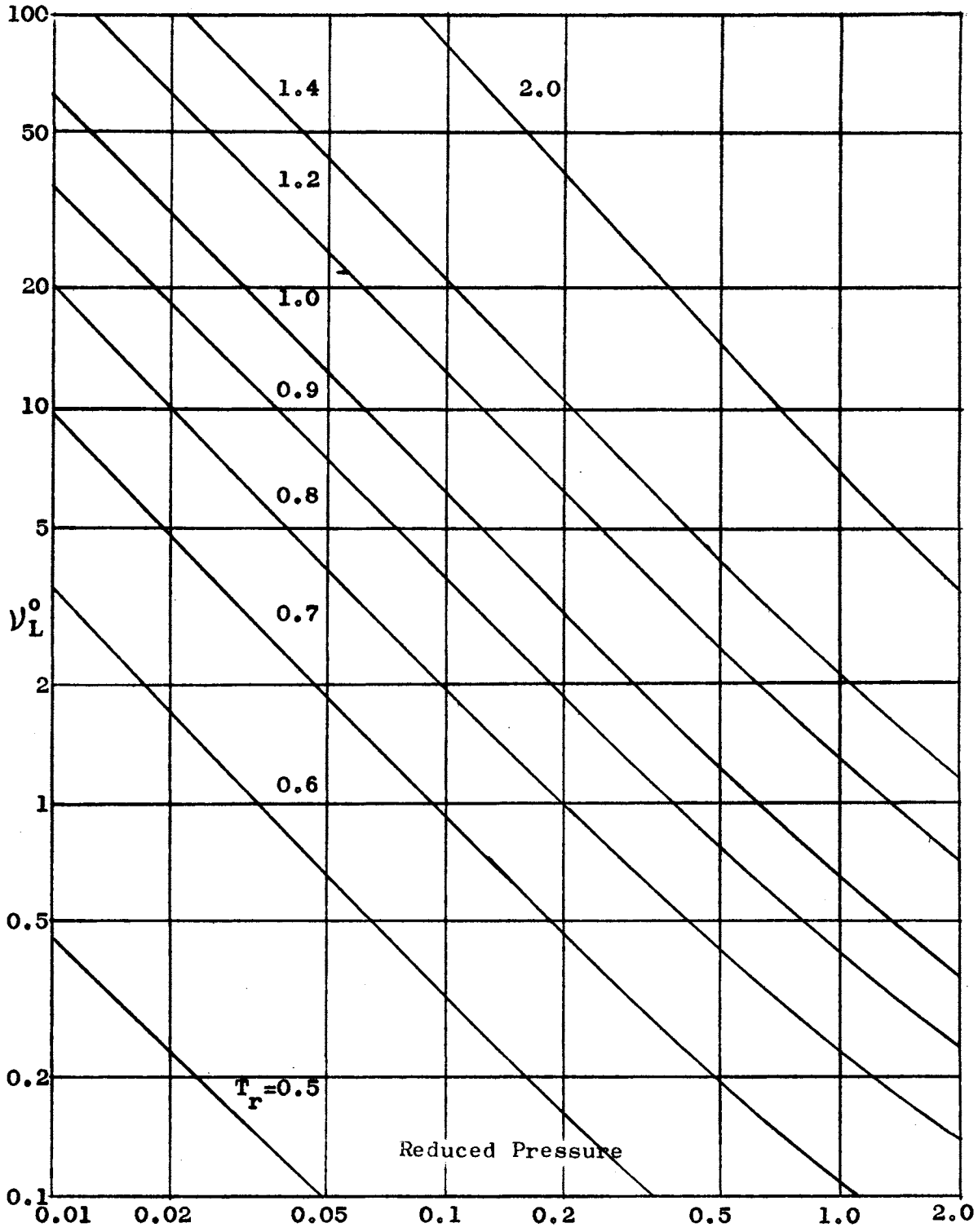

Figure 5

Smoothed Values of Fugacity Coefficients for Pure Simple Liquids

(24)

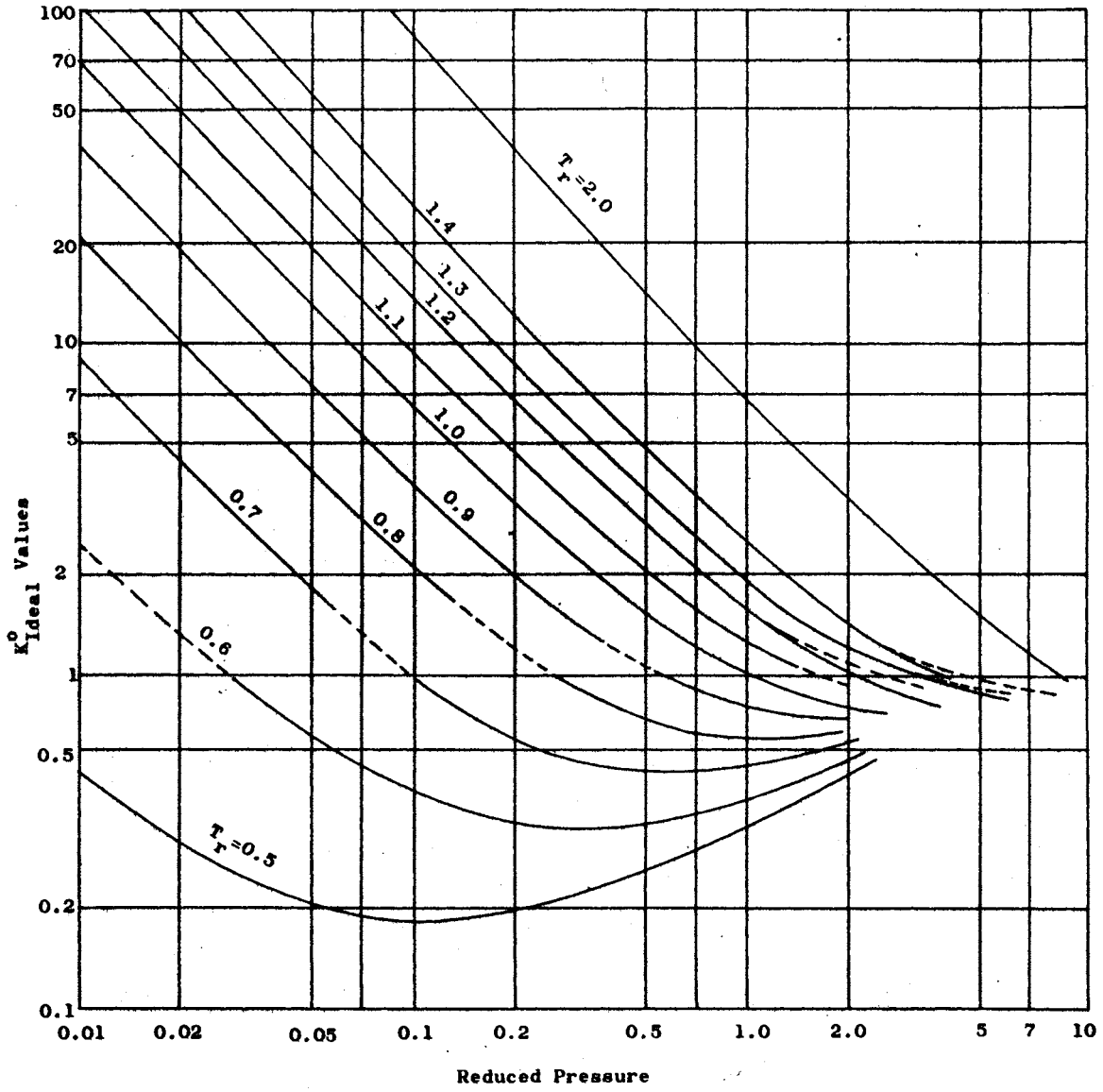

Figure 6

Smoothed K°_{Ideal} through K' Relationship

$$K' = \frac{\nu'}{(f/P)'} \qquad \text{(III-7)}$$

where:

$$\nu = \nu^{o} (\nu')^{\omega} \qquad \text{(III-8)}$$

$$f/P = (f/P)^{o} \left((f/P)'\right)^{\omega} \qquad \text{(III-9)}$$

Values of K' were calculated using Equation III-7 and the previously noted sources of ν' and $(f/P)'$. These were tested together with the values of K^{o} from the plot of K^{o} vs. T_r and P_r (Figure 6) at the vapor pressure at various acentric factors. It was concluded that these values of K' were not satisfactory since the unity K-value requirement was not satisfied at the vapor pressures. Even though the K-values calculated in this manner did not satisfy the vapor pressure requirement, they did suggest K' to be a function of reduced temperature only.

The requirement that K = 1.0 at the vapor pressure was the basis used for the K' correlation shown in Figure 7. The procedure used in obtaining values for this correlation and for obtaining the smoothed K^{o} correlation, shown as the dashed portion of Figure 6, is outlined in Appendix G. A sample calculation illustrating the method is also included. Results of the calculations using this procedure are tabulated in Table XXVI.

The technique used in developing the above K^{o} and K' correlations is limited in range of application and it was found not adequate for the lower reduced temperature and higher reduced pressure regions. It was necessary to use another method to complete the ideal K-value correlation. Thus the simultaneous study of two other methods was begun: (1) the development of an ideal

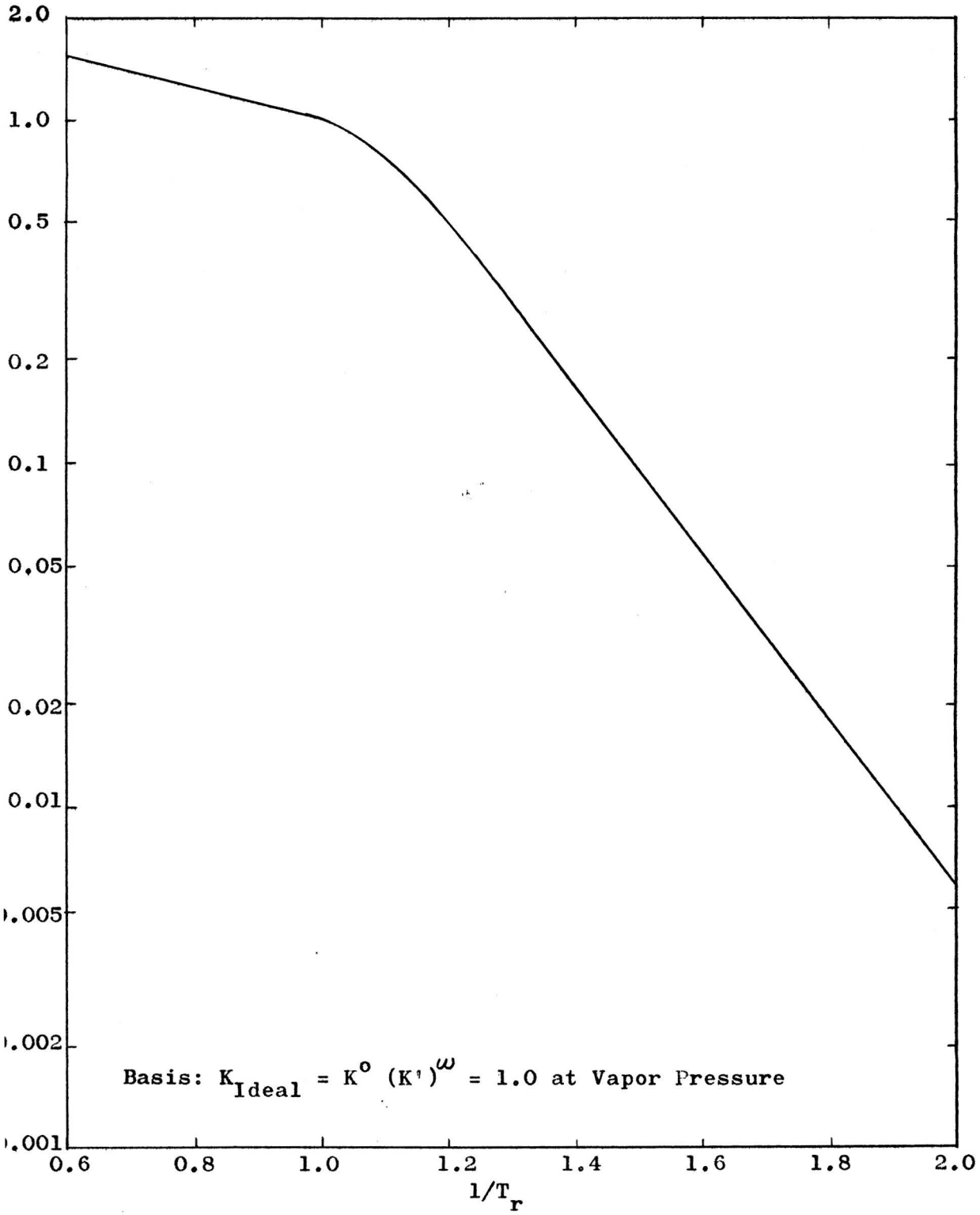

Figure 7

Correction Factor - K' versus $1/T_r$ (25)

K-value correlation from experimental x-y data discussed in Chapter IV and (2) the 'imperfection pressure correction' approach discussed in Chapter V.

The Hougen K-Value Correlation

Hougen and co-workers (38) developed a generalized three parameter ideal K-value correlation from PVT data (Figure 8). The three parameters were reduced pressure, reduced temperature and the critical compressibility factor. The correlation chart published by Hougen (38) was for a critical compressibility factor of 0.27. The critical compressibility factor and the acentric factor are related by the following equation

$$Z_c = (0.293) - (0.078)\omega \qquad \text{(III-10)}$$

With the relationship between the acentric factor and the critical compressibility factor available, it is possible to convert the Hougen K-values to a zero acentric factor basis by the use of vapor pressure ratios as follows

$$\left(K_{Ideal}\right)_{\omega=0} = \left(K_{Ideal}\right)_{Z_c=0.27} \left(\frac{\left(p_r^o\right)_{\omega=0}}{\left(p_r^o\right)_{Z_c=0.27}}\right) \qquad \text{(III-11)}$$

The Hougen K-values were converted to the zero acentric factor basis using Equation III-11. The resulting K-values are presented in Figure 9.

A comparison of Figures 6 and 9 shows that the Hougen ideal K-values for the simple fluid are lower than the values obtained

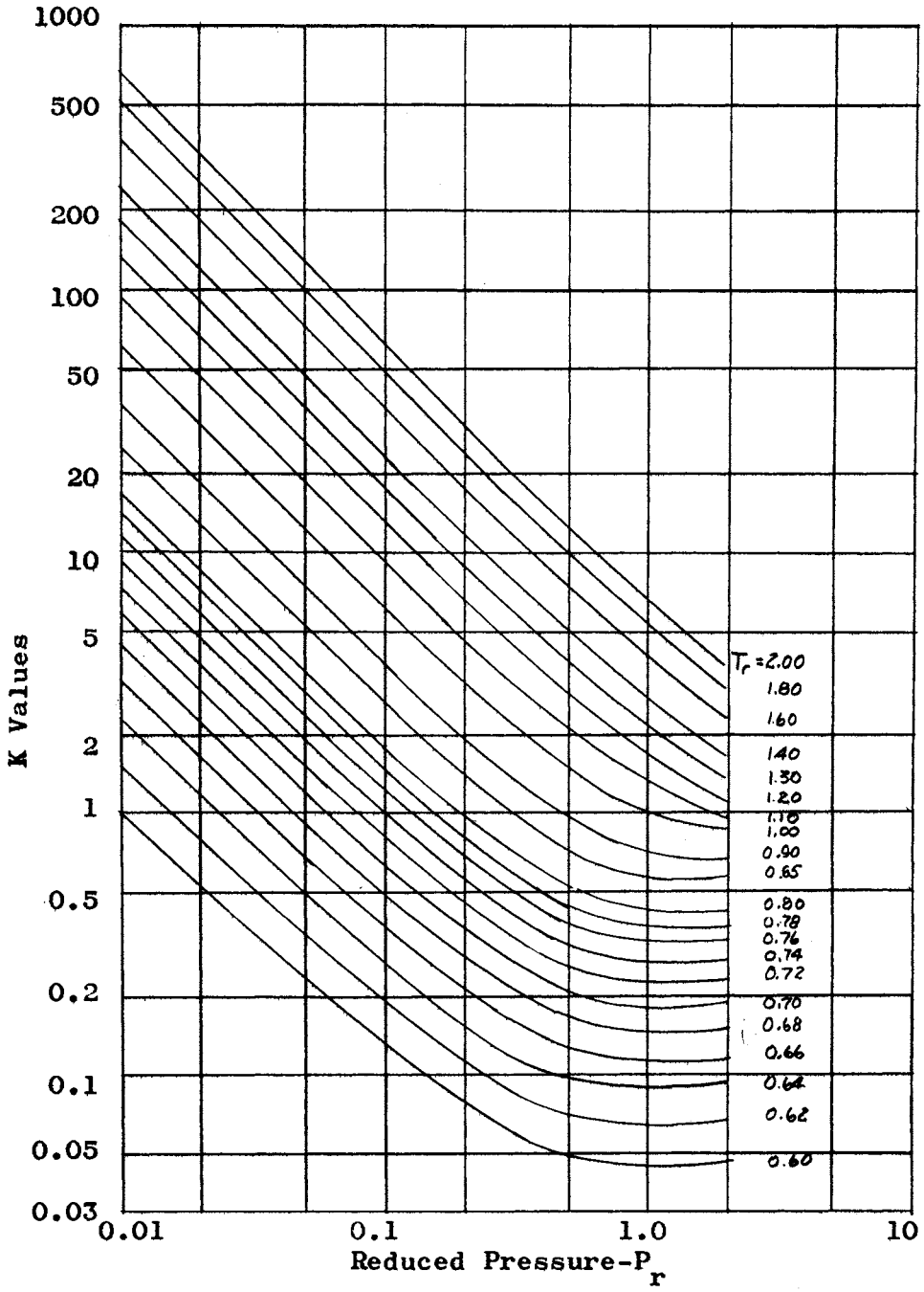

Figure 8

Hougen Vaporization Equilibrium Constant-K
(Z_c=0.27)(38)

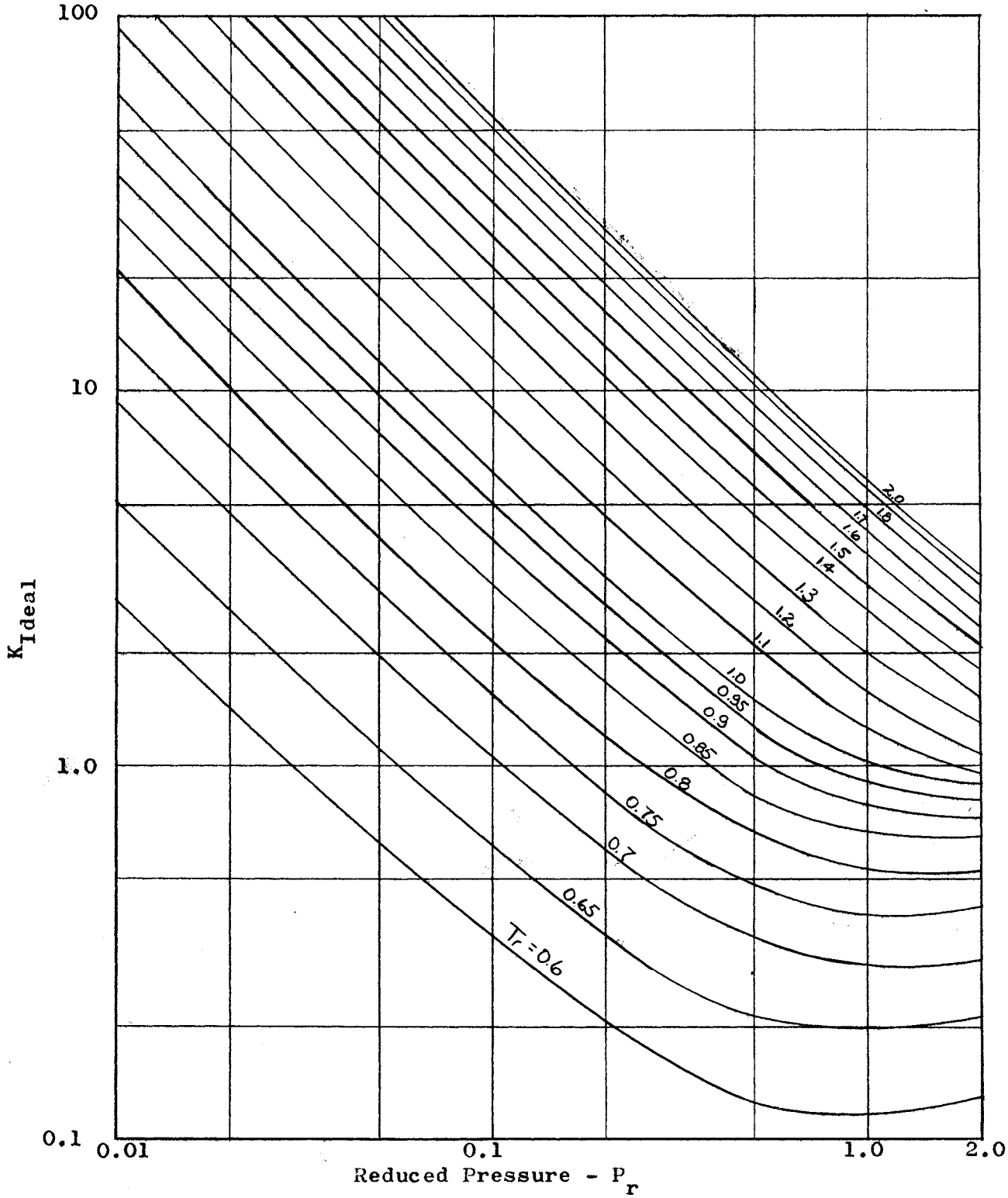

Figure 9

Hougen Ideal K-Values for Simple Fluid (24)

from the modified f/P correlations. The greatest deviation occurs at the lower reduced temperatures. There is good agreement between the two correlations in the region of high reduced pressure and high reduced temperature.

CHAPTER IV

IDEAL FUGACITIES FROM EXPERIMENTAL VAPOR-LIQUID EQUILIBRIA DATA

Ideal K-values, including their K^{o} and K' components, were evaluated from experimental vapor-liquid equilibria data by a method similar to that used by Hoffman, et al. (37) in their evaluation of standard state fugacities of hypothetical vapors from vapor phase activity coefficients. The method used here differs only in a few details from that of Hoffman, et al. These differences will be pointed out as the discussion progresses.

The data of three binary systems were selected, namely, the mixtures of methane-ethane (11), ethane-n-butane (43) and ethane-n-heptane (42). These systems were chosen because the heavy components covered a wide range of acentric factors, 0.105 to 0.352, and because ethane appeared in these mixtures both as solute and solvent. Hoffman et al. used the data of the binary systems methane-propane (1,73), ethane-n-pentane (67), ethane-benzene (44), propane-n-pentane (74) and propane-benzene (31).

Prior to making any calculations it was necessary to plot the experimental data on large scale coordinates to permit the reading of x and y values along several isotherms at uniform pressure intervals. This preliminary data processing was necessary because the calculations were to be made and the results plotted at iso-

thermal conditions.

Vapor Phase Analysis

Fugacity coefficients were calculated for the light component in the pure vapor state and in the mixture at the system temperature and pressure. The fugacity coefficients were evaluated using the equations of state of Black (10), Redlich-Kwong (68) and Benedict-Webb-Rubin (7). Calculations were made at the values of pressure, temperature and composition corresponding to the experimental points. The actual calculations were carried out using the IBM 650 computer programs of Stuckey and Thompson (84, 85).

Vapor phase activity coefficients were then computed from these fugacity coefficients as follows

$$\ln \gamma_i^V = \ln \bar{f}_i^V / Py_i - \ln f_i^V / P = \ln \bar{f}_i^V / f_i^V y_i \quad \text{(IV-1)}$$

Typical results of such calculations are presented in Figure 10. Here the log of the vapor activity coefficient is plotted against mole fraction for ethane of the ethane-heptane binary at 250°F. Two features of this plot deserve comment, namely: (1) the wide spread between the curves for the three different equations of state and (2) the upturn of the curves between 0.80 and 0.92 mole fraction ethane in the region where the system pressure is the highest.

The spread in the curves in Figure 10 is probably due to the different combination rules used for the individual component constants in the different equations of state. There is no apparent

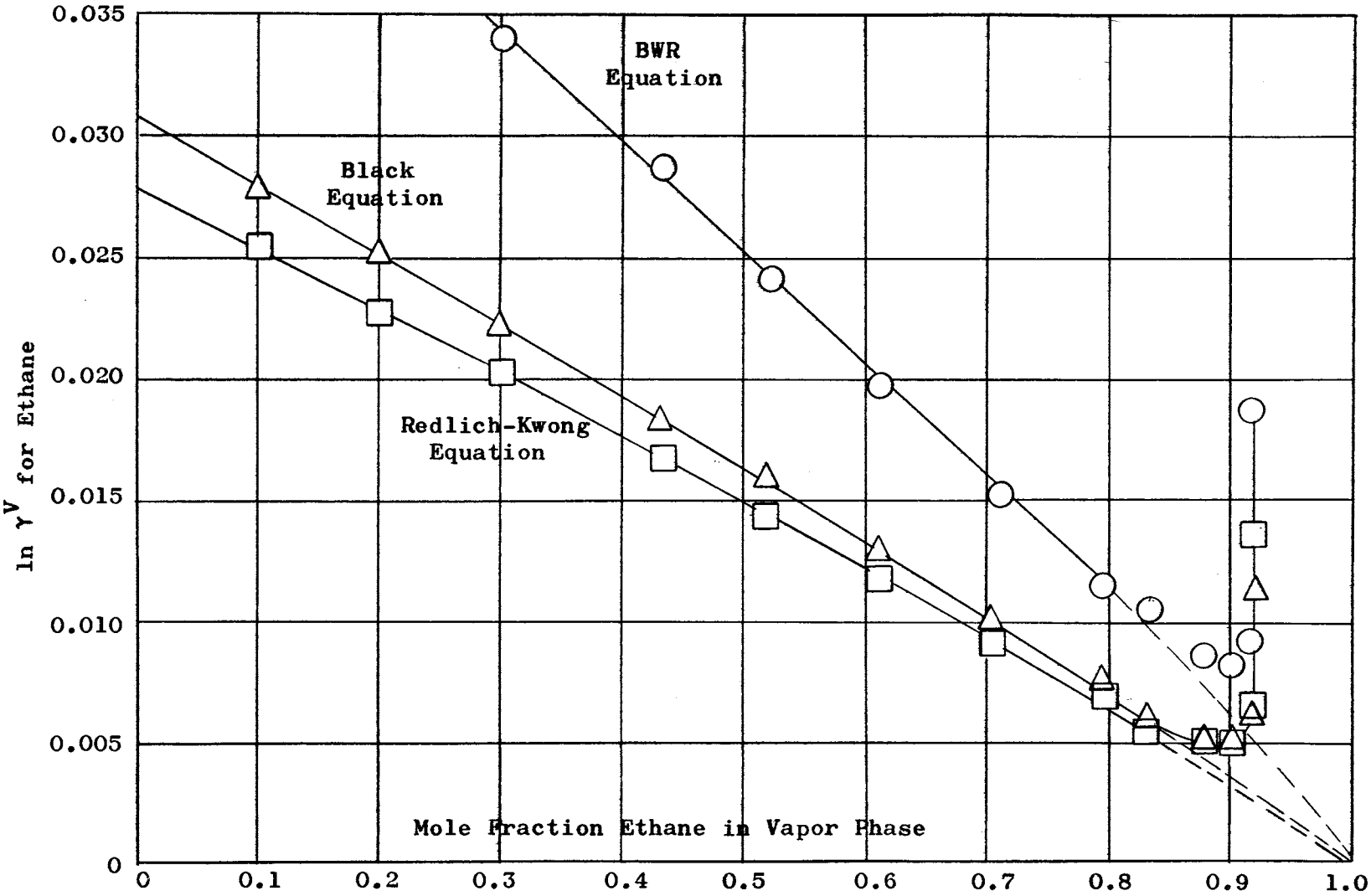

Figure 10

Activity Coefficients of Ethane in Ethane-n-Heptane Mixture (23)

reason to choose one equation of state over another. The Black and the Redlich-Kwong equations offer simplicity, the Black being the simpler of the two since it is already in generalized form. Black's equation,which is limited to an upper pressure of 0.9 to 0.95 of the critical pressure, was developed for vapors whereas the Redlich-Kwong equation was developed for gases. The Black equation gives negative values for the compressibility factor at high pressures. From a practical standpoint the R-K equation would be the best, at least where $T_r \geq 1.0$ for the light component. The Black equation was chosen for this work since it was the equation that Hoffman et al. (37) had used in their work.

The plots of $\ln \gamma^V$ vs. mole fraction based on all of the equations of state studied showed the upturn at high ethane mole fraction seen in Figure 10. This phenomenon has been observed in investigations of other binary systems. The upturn cannot be attributed to the equations of state themselves, but rather to the approach of the phase boundary between liquid and vapor phases.

The upturn of Figure 10 begins at approximately 0.82 mole fraction where the rate of increase of mole fraction with increasing pressure on the phase diagram begins to decrease. The upturn becomes a maximum at the point on the phase diagram where the rate of increase of mole fraction with pressure is zero.

At 250°F. it is not possible for ethane in the ethane-n-heptane system to exist at mole fractions greater than 0.916 for two phase systems. This can be seen by referring to the phase diagram for the ethane-n-heptane system (42).

Smooth curves that extrapolated to $\ln \gamma^V = 0$ at $y = 1.0$ were

drawn to represent the γ^V vs. y relationship for ethane in n-heptane at 250°F. These curves are shown as dashed lines in Figure 10.

The activity coefficient for the dissolved component, i.e., the component in the hypothetical state, can be found through use of the Gibbs-Duhem (39) relationship. The Duhem equation is commonly applied to binary liquid-vapor systems at equilibrium and is used widely in the calculation of the composition of the coexisting phases of binary systems.

The rigorous form of the Gibbs-Duhem equation at constant temperature is (39)

$$\frac{d \ln \gamma_1}{d \ln y_1} - \frac{d \ln \gamma_2}{d \ln y_2} = \frac{V_m}{RT} \frac{dP}{dy_1} \qquad \text{(IV-2)}$$

Theoretically, this equation applies only to a process carried out at constant temperature and pressure on the liquid phase. In most mixtures encountered in vapor-liquid equilibria, if one varies the composition at constant temperature, the total pressure also varies and Equation IV-2 is not strictly applicable. This equation would apply for the constant temperature case if some method other than the vapor pressure were employed to exert pressure on the liquid which was adjusted to keep the total pressure constant (71). For isothermal data, as was used in this study, the constant temperature-pressure Gibbs-Duhem equation is often an excellent approximation, especially at moderate pressures.

For this work, the following short form of the Gibbs-Duhem equation was used to calculate the vapor activity coefficient for the heavy component by numerical integration

$$\ln \gamma_2^V = \int_{y_1=y_2}^{y_1=0} (y_1/y_2)\, d \ln \gamma_1^V \qquad \text{(IV-3)}$$

Figure 11 shows the smoothed result of the integration of the 250°F. isotherm for the ethane-n-heptane binary.

The dashed portion of the curves refers to the extrapolated portion of Figure 10, i.e., the region outside the boundary of the phase diagram. The dashed portion of the curves, therefore, represents an unreal state.

Hoffman et al. (37) obtained vapor activity coefficients for the less volatile component of binary mixtures through use of the van Laar equation, a particular solution to the Duhem equation.

$$\log \gamma_i^V = \frac{a_{ij}^2}{\left(1 + a_{ij}^2 y_i / a_{ji}^2 y_j \right)^2} \qquad \text{(IV-4)}$$

Equation IV-4 was fitted to the isothermal vapor phase activity coefficients of the light component of each of the binary mixtures studied. The a_{ij}^2 constants were then used to calculate the isothermal vapor phase activity coefficients for the heavy component of the binary mixtures.

The results obtained using Equation IV-3 are in excellent agreement with those via Equation IV-4. Application of the numerical integration procedure is straight-forward and yields accurate results with less effort than the Hoffman procedure. The numerical integration procedure is, therefore, the preferable method for 'bridging over' from the activity coefficient of the

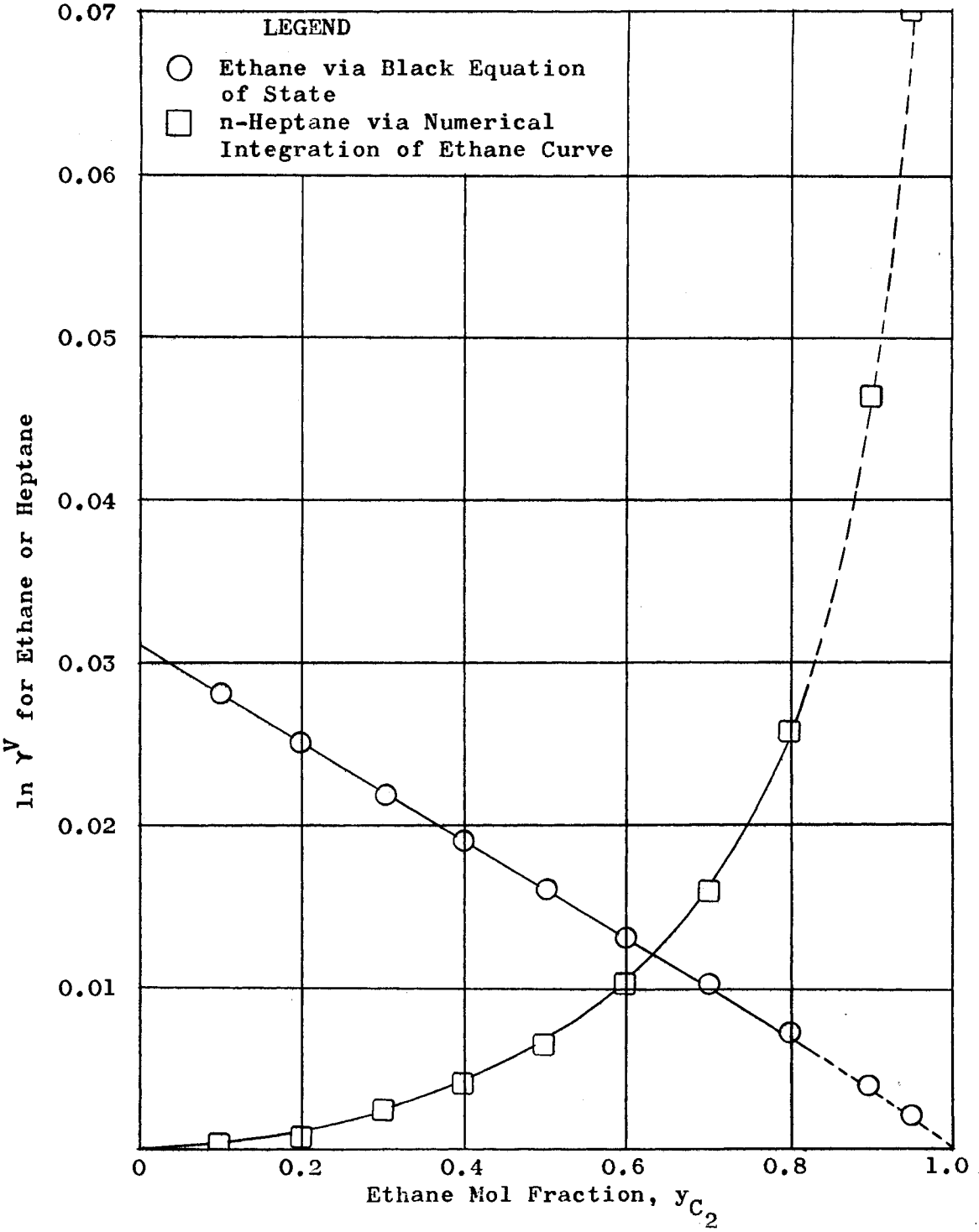

Figure 11

Activity Coefficients of Ethane and n-Heptane in Equilibrium Vapor of C_2-n-C_7 Binary at 250°F. (23)

light component to the vapor activity coefficient of the heavy component. This procedure is applicable only when x-y data is available for the entire composition range.

The γ^V values derived in this way for the heavy component of the mixture were used in the calculation of the corresponding (f^V/P) values. This calculation was made by dividing the γ_H^V value by the ϕ_H^V (i.e., $(\bar{f}^V/Py)_H$) value computed by the Black equation for the same component at the same conditions. This calculation, which is made by Equation IV-1, gives an (f^V/P) value for a hypothetical vapor. This is because the heavy component can exist only as a liquid in the pure state at the pressure involved.

In this manner the f/P ratios were computed for the heavy components of the three binaries studied, giving values for ethane, n-butane and n-heptane as hypothetical vapors. A comparison of the n-butane values with the results Hoffman et al. reported for $Z_c = 0.27$ is given in Table I.

The f/P values compared in Table I show the agreement of the Hoffman method and the method used in this work. The Hoffman, et al. values were based on their calculations for propane, n-pentane and benzene.

The hypothetical $(f/P)_V$ values for the heavy components of the methane-ethane, ethane-n-butane and ethane-n-heptane binaries were used to prepare plots of ln f/P vs. ω. The best straight lines were drawn through the points and were extrapolated to $\omega = 0$ to get the values of $(f/P)_V^o$. These values are plotted as a function of reduced temperature and pressure in Figure 12.

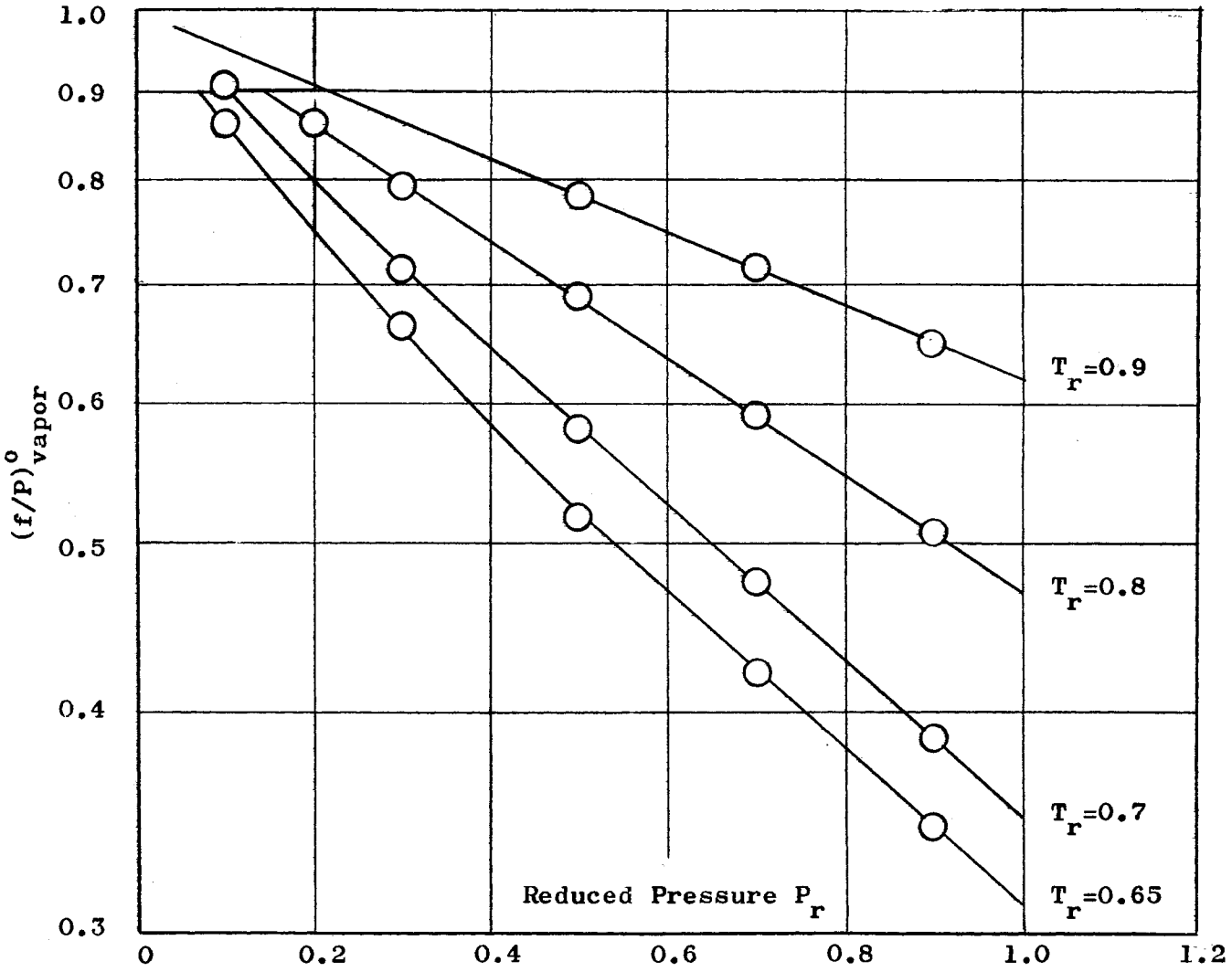

Figure 12

Fugacity Coefficient for Pure Simple Fluid in Hypothetical Vapor State (23)

TABLE I

COMPARISON OF HYPOTHETICAL f/P VALUES

T_r	P_r	$(f/P)_{HV}$ Hoffman et al. $Z_c = 0.27$ $\omega = 0.2925$	$(f/P)_{HV}$ This Work n-Butane $Z_c = 0.274$ $\omega = 0.201$
0.7	0.4	0.66	0.68
	0.6	0.53	0.58
	0.8	0.44	0.49
0.8	0.4	0.76	0.75
	0.6	0.66	0.66
	0.8	0.57	0.58
0.9	0.6	0.73	0.73
	0.8	0.66	0.66

The hypothetical $(f/P)^o$ values from Figures 4 and 12 are compared in Table II.

TABLE II

COMPARISON OF HYPOTHETICAL f/P VALUES FOR THE SIMPLE FLUID

		$(f/P)^o$ for Hypothetical Vapor	
T_r	P_r	Pitzer-Prausnitz Values Figure 4	Ideal Fugacities Figure 12
0.7	0.4	0.46	0.65
	0.6	0.33	0.53
	0.8	0.26	0.43
0.8	0.4	0.66	0.74
	0.6	0.53	0.63
	0.8	0.43	0.55
0.9	0.4	0.78	0.82
	0.6	0.68	0.75
	0.8	0.59	0.68

Figure 4 presented the composite of the $(f/P)^o$ values of

Pitzer et al. (51) at $T_r \geq 1.0$ and the modified hypothetical vapor state $(f/P)^o_V$ values of Prausnitz (66) for $T_r < 1.0$.

There is a large difference between the $(f/P)^o$ values for the hypothetical vapor from these two sources. Yet there is good agreement between the $(f/P)_V$ values of Hoffman, et al. and the $(f/P)_V$ values for butane obtained in this work. The difference between the values compared becomes greater at the higher pressures.

Gamson and Watson (28) obtained a generalized correlation for the fugacity coefficients of several gases in the real state and extrapolated the fugacity coefficient curves into the hypothetical region. Smith and Watson (80) revised the extrapolations of Gamson and Watson.

Hoffman et al. (37) found in comparing their values with those of Gamson and Watson (28) that the Hoffman values were larger and also that the difference between the values compared was larger at the higher pressures.

One concludes that the $(f/P)^o_V$ values presented in Figure 4 are low and that probably the $(f/P)^o_V$ values obtained via the modified Hoffman procedure are high. The modified Hoffman procedure should be applied to additional experimental data before a definite conclusion is made.

The method described above is better understood by following a step by step outline. Such an outline together with a sample calculation is presented in Appendix J.

Liquid Phase Analysis

The activity coefficients for the components in the hypothetical liquid phase can be obtained in a manner similar to that used to obtain the hypothetical vapor activity coefficients. This method, although not used in this work, will be outlined below:

1. The fugacity coefficient for the heavy component in the vapor is calculated via an equation of state. The fugacity coefficient for the heavy component in the liquid is obtained from the criterion of equilibria

$$\bar{f}_i^V = \bar{f}_i^L \qquad \text{(IV-5)}$$

2. The fugacity coefficient of a pure substance in the real liquid state can be obtained from the generalized correlation of either Pitzer, et al. (20) or Hougen, Watson and Ragatz (38).

3. The liquid activity coefficient for the heavy component is calculated as follows

$$\gamma_H^L = \frac{\bar{f}_H^L}{Px_H} \frac{1}{(f/P)_H} = \phi_H^V \frac{y_H}{x_H} \frac{1}{(f/P)_H} \qquad \text{(IV-6)}$$

where

$$\frac{f_H^L}{Px_H} = \frac{\phi_H^V y_H}{x_H} \qquad \text{(IV-7)}$$

4. A plot of $\ln \gamma_H^L$ is made as a function of the mole fraction of the heavy component. This curve is integrated numerically to obtain γ_L^L for the light component. The

integration can be performed only if x-y data is available over the entire composition range.

5. The f_L^L for the hypothetical liquid state is calculated as follows

$$f_L^L = \frac{\bar{f}_L^L}{x_L} \frac{1}{\gamma_L^L} \qquad \text{(IV-8)}$$

γ_L^L is obtained from step 4 above. $\bar{f}_L^L$ is obtained from an equation of state using the equilibrium criterion of Equation IV-5.

The values obtained in step 5 above can be used to prepare generalized plots of hypothetical liquid fugacities. In turn the ideal K-values for the real and hypothetical states can be calculated as the ratio of the liquid and vapor fugacities.

Ideal K-Values

Ideal K-values were calculated for ethane, n-butane and n-heptane as the ratio of the fugacity in the pure liquid state to the fugacity in the hypothetical vapor state

$$K_{Ideal} = \frac{f_i^L/p_i^o}{f_i^V/P} \frac{p_i^o}{P} = \frac{p_i^o}{P} \frac{(f_i^V/p_i^o)\, e^{\frac{V^L(P-p_i^o)}{RT}}}{(f_i^V/P)} \qquad \text{(IV-9)}$$

The Black (10) equation of state was used to evaluate (f_i^V/p_i^o) at the vapor pressure of the light component for the numerator in the equation above. This fugacity/pressure ratio is corrected

from the vapor pressure to the system pressure by the exponential term which is known as the Poynting correction. The (f_i^V/P) values for the denominator in Equation IV-9 are the hypothetical values obtained as described above.

The ideal K-values obtained via Equation IV-9 are plotted in Figure 13 for ethane, Figure 14 for n-butane and Figure 15 for n-heptane. These ideal K-values were fitted to the following equation

$$K_{Ideal} = K^{o} \, (K')^{\omega} \qquad \text{(IV-10)}$$

The K^{o} values obtained in this way are presented in Figure 16 as a function of reduced temperature and reduced pressure. Values of K' are presented in Figure 17. These ideal K-values will be compared with ideal K-values from other sources in Chapter VII.

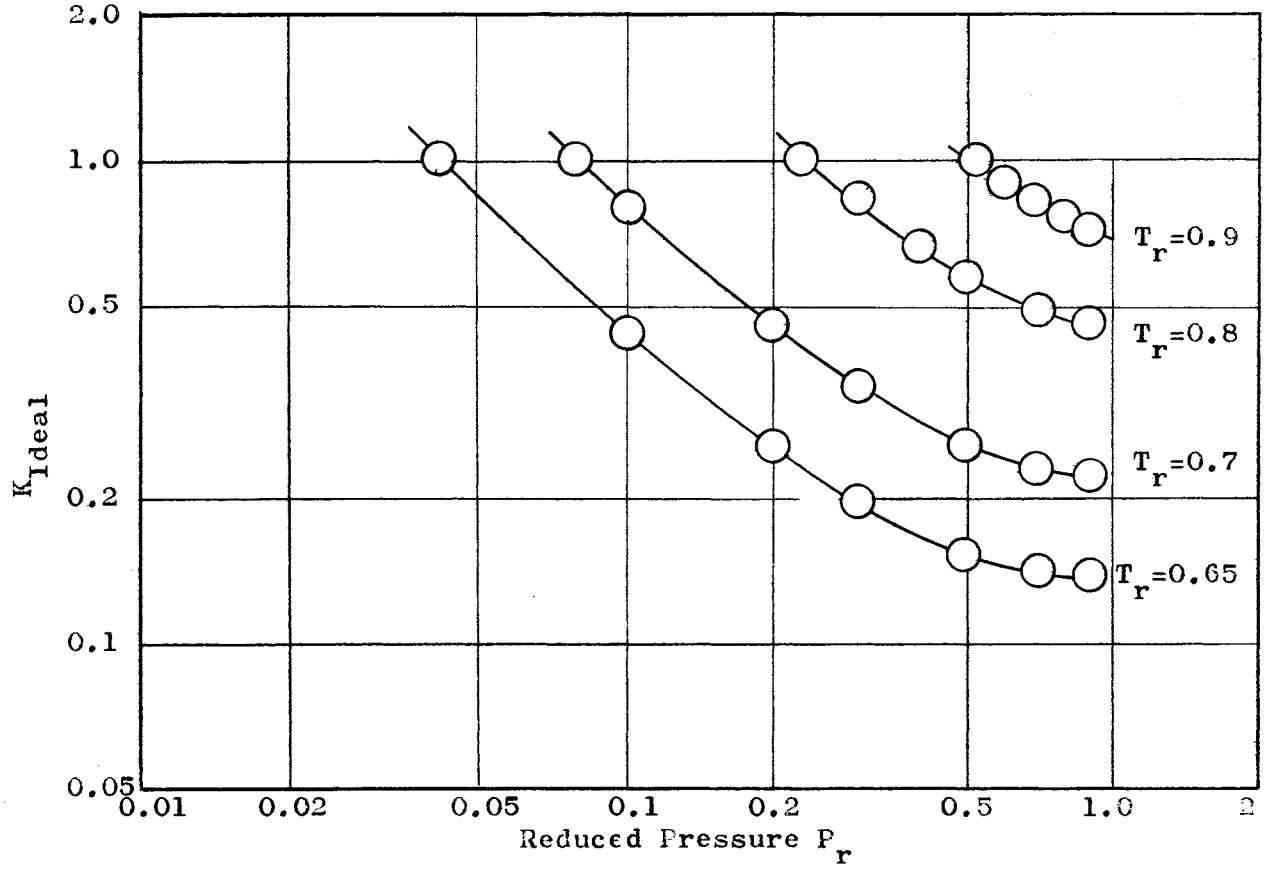

Figure 13

Ideal K-Values for Ethane, Derived from

Methane-Ethane Data (23)

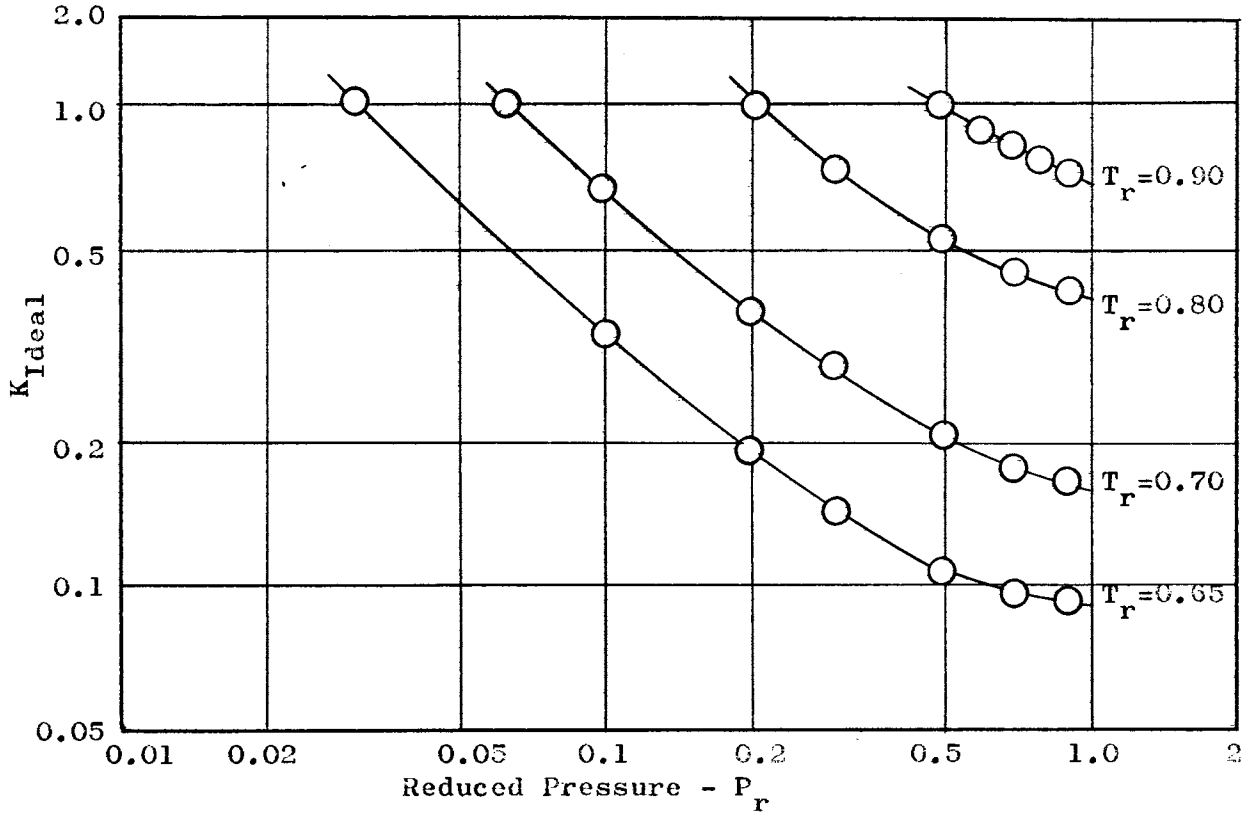

Figure 14

Ideal K-Values for n-Butane, Derived from Ethane-n-Butane Data (23)

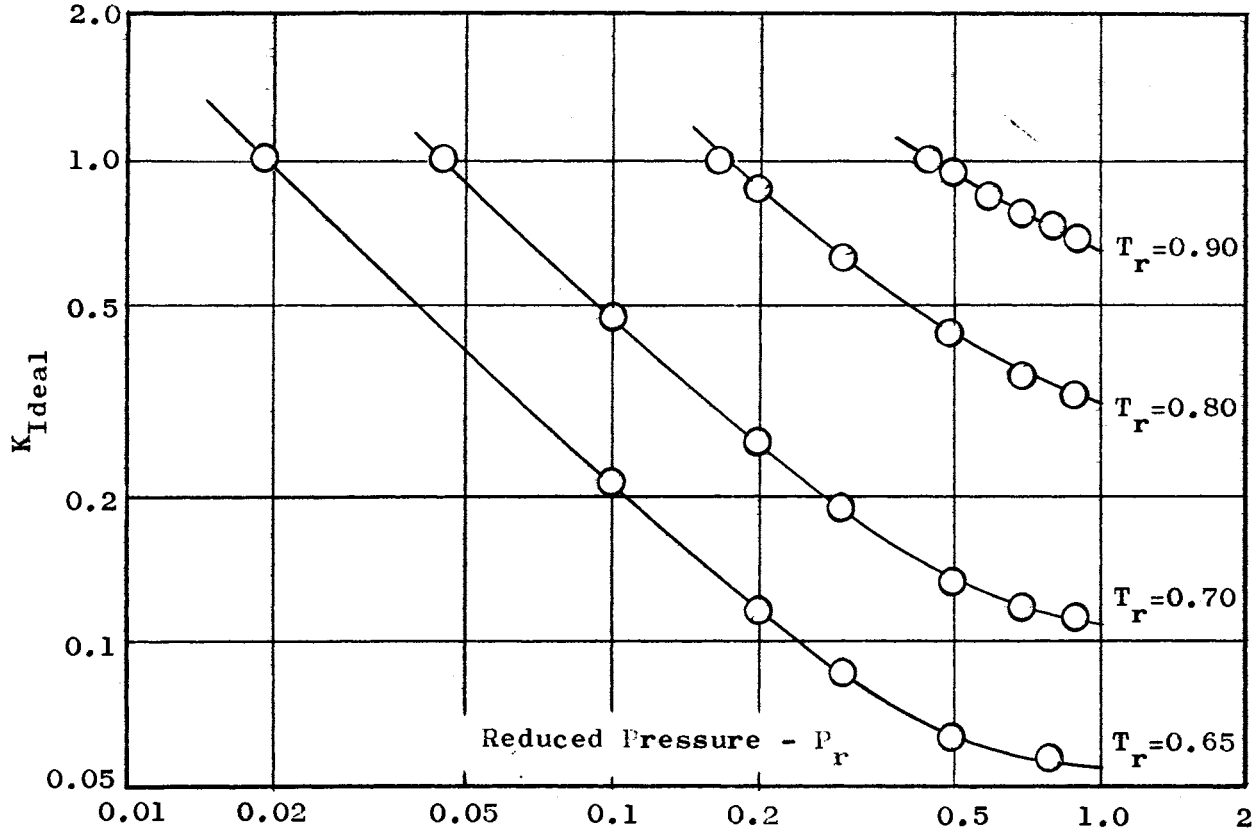

Figure 15

Ideal K-Values for n-Heptane, Derived

From Ethane-n-Heptane Data (23)

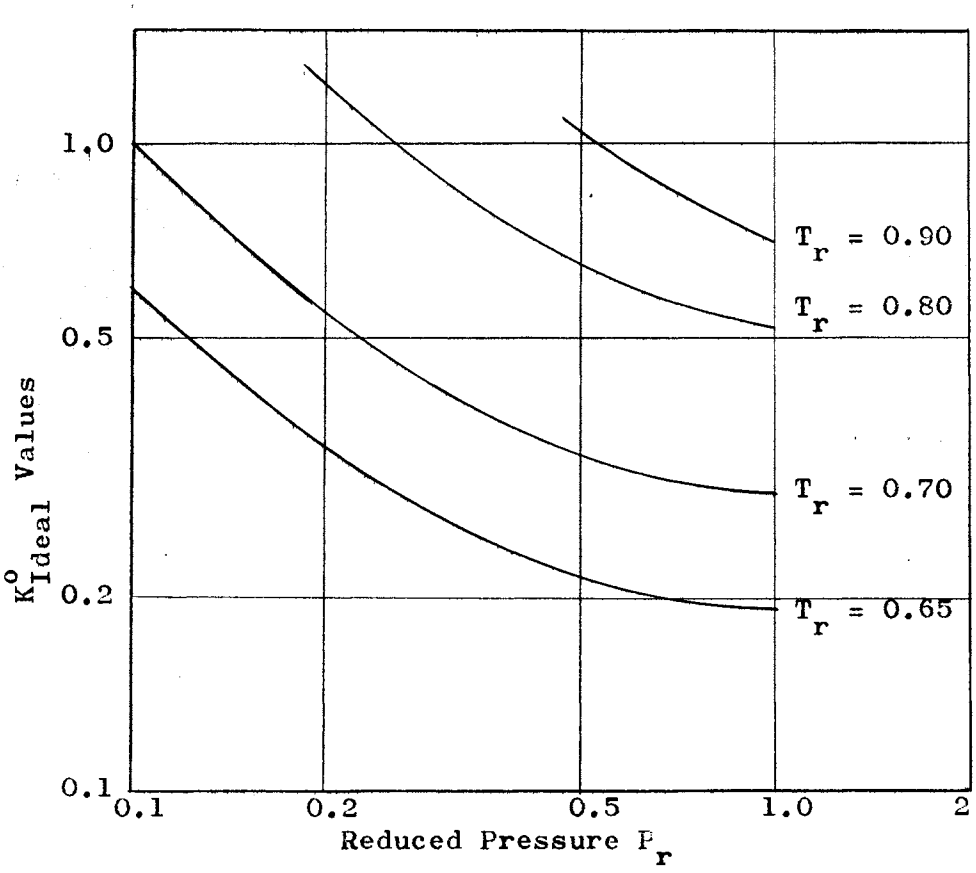

Figure 16

Ideal K-Values for Simple Fluid; Derived from x-y Data by Calculations (23)

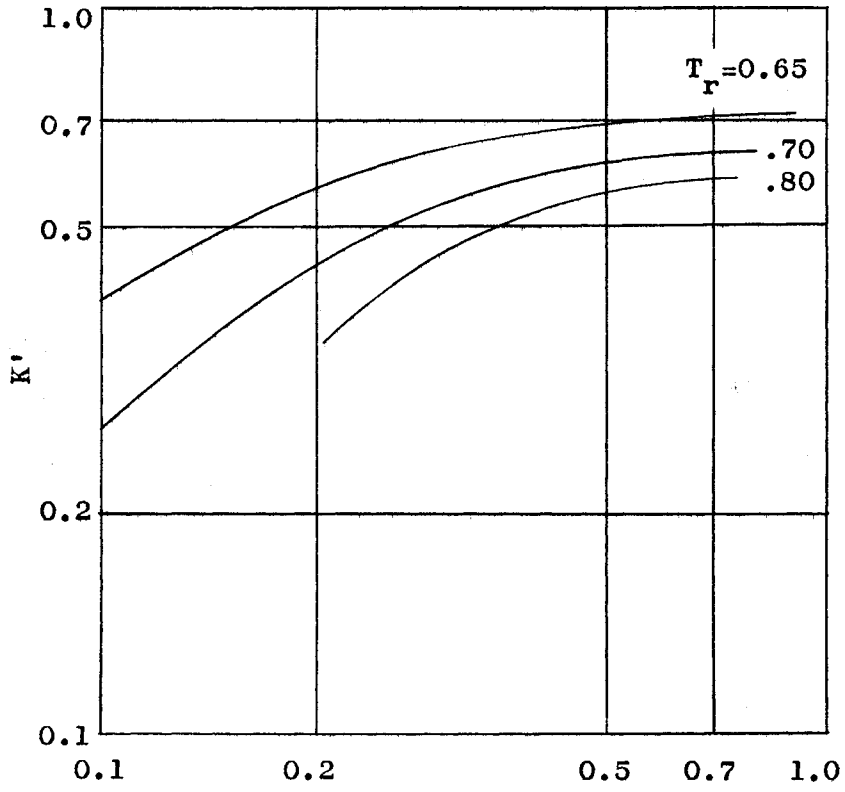

Figure 17

K' Values-Derived from x-y

Data by Calculations

CHAPTER V

IMPERFECTION PRESSURE CORRECTION APPROACH

General Background

The 'so-called' imperfection pressure correction is defined as

$$\theta = \frac{K_{Raoult's}}{K_{Ideal}} = \frac{p_i^o/P}{f_i^L/f_i^V} \qquad (V\text{-}1)$$

where:

p_i^o = vapor pressure

P = system pressure

f_i^L = fugacity of the pure component as liquid at the system temperature and pressure

f_i^V = fugacity of the pure component as vapor at the system temperature and pressure

Historically, K-values were first defined in terms of Raoult's law. Raoult's law, however, was not adequate for situations where the vapor phase did not behave as a perfect gas. The fugacity concept was introduced to correct for the non-ideality of the vapor phase.

'An ideal solution is one in which the fugacity of each component is proportional to the mole fraction of that component at every temperature and pressure'(51). If the liquid and vapor

mixtures are regarded as ideal solutions, the fugacity of each component is equal to the product of the mole fraction and the fugacity of the pure component in a like phase at the same temperature and pressure (Lewis and Randall rule). The general equation for the equilibrium then becomes

$$f_i^L x_i = f_i^V y_i \qquad \text{(V-2a)}$$

The vapor-liquid equilibrium constant, K, for a component of an ideal solution is obtained by rearranging Equation V-2a

$$K = \frac{y}{x} = \frac{f_i^L}{f_i^V} \qquad \text{(V-2b)}$$

Equation V-2b is the basic relationship evaluated in preparing the MIT (52) and the Michigan (12) K-charts. These two K-value correlations are discussed in detail in Chapter II.

The development of both of these correlations neglected the effects of pressure on the liquid phase. These correlations did little more than correct partially for the non-ideal behavior of the gas phase.

When the mixture under the system conditions cannot be considered ideal, some procedure must be utilized for taking into account gas law deviations and the effects of pressure on the liquid.

The imperfection pressure correction, Θ, was defined to permit evaluation of correction factors to be applied to the Raoult's K-value.

Benedict et al. (6) expressed the distribution coefficient

for the case where deviations from the perfect gas laws are relatively small so that only the second coefficient of the virial equation of state need be considered

$$\ln (y_i/x_i) = \ln (p_i^o/P) + (P-p_i^o)(V-B')/RT + \ln \gamma_i \quad (V-3)$$

where: $(P-p_i^o)(V-B')/RT$ = a correction for the non-ideal behavior of the vapor phase.

B' = the second virial coefficient in the Berlin virial equation of state

V = the molar volume

Equation V-3 can be rearranged to the following form

$$\ln \gamma_i = \ln (Py_i/p_i^o x_i) - (P-p_i^o)(V_i-B')/RT \quad (V-4a)$$

$$\gamma_i = \Theta_i Py_i/p_i^o x_i \quad (V-4b)$$

where: $\Theta_i = \exp (p_i^o-P)(V_i-B')/RT$

Equation V-4a may also be obtained from Equation 10 of Scatchard and Raymond (78) where their δ may be considered to be zero. Equation V-4b was used in the studies of Colburn, et al. (29,56) and was applied to both binary and ternary mixture data.

It should be noted that Θ equals unity when the total pressure equals the vapor pressure since Equation V-4 employs the saturated vapor as the reference state. Values of Θ are a maximum when the total pressure is zero.

Scheibel (79), using the Wohl (92) equation for the second

virial coefficient and the Meissner-Redding (55) equation for the molar liquid volume, reduced the Benedict et al. equation for Θ to an equation in terms of P_c, T_r and the difference between the vapor pressure of the pure component and the total pressure of the system. The resulting equation has been constructed on a set square type nomograph in which the imperfection pressure correction is obtained by a single setting of the other three variables. The application of this nomograph is limited due to the narrow range of the variables covered.

Black (10) has derived an equation for the imperfection pressure correction in terms of his 'approximate' equation of state. This Θ equation is applicable to low pressure differences $(P-p_i^o)$ and to moderate pressures in general.

Basic Equations

From the definitions of fugacity and the criteria for vapor-liquid phase equilibria, we can write

$$K_i = \frac{y_i}{x_i} = \frac{\bar{f}_i^L/x_i}{\bar{f}_i^V/y_i} = \frac{\bar{f}_i^L/f_i^L x_i}{\bar{f}_i^V/f_i^V y_i} \frac{f_i^L/p_i^o}{f_i^V/P} \frac{p_i^o}{P} = \frac{\gamma_i^L}{\gamma_i^V} \frac{1}{\Theta} \frac{p_i^o}{P} \qquad (V\text{-}5)$$

where: γ_i^L and γ_i^V are activity coefficients expressing departure from ideal solutions or mixtures in liquid and vapor phases

$$\Theta_i = \frac{f_i^V/P}{f_i^L/p_i^o} = \text{the imperfection pressure correction} \qquad (V\text{-}5a)$$

(f_i^V/P) = the fugacity/pressure ratio for pure vapor at the system conditions (P and T)

(f_i^L/p_i^o) = the fugacity/pressure ratio for pure liquid at the system conditions (i.e., fugacity at P and T divided by vapor pressure at T)

$(p_i^o/P) = K_{Raoult}$

$K_{Ideal} = 1/\Theta_i K_{Raoult}$

The imperfection pressure correction term can be found from PVT data or an equation of state starting with the following

$$\ln (f_i^V/P)_P = \int_{p^o}^{P} (V_i^V - \frac{RT}{P})\, dP \qquad (V\text{-}6)$$

and $$\ln (f_i^L/p_i^o)_P = \ln (f_i^V/P)_{p_i^o} + \frac{1}{RT}\int_{p_i^o}^{P} V_i^L\, dP \qquad (V\text{-}7)$$

The two equations above are for isothermal conditions and for pure components.

Equation V-6 is a familiar expression derived in all thermodynamics texts. Therefore, its derivation will not be included here. Equation V-7 expresses the liquid fugacity ratio in terms of the value of the saturated vapor f/P value, at the same temperature, and a liquid volume correction for the difference between the system and vapor pressures. The term which corrects the fugacity from the vapor pressure to the system pressure is called the 'Poynting effect'.

We can rewrite the expression for Θ_i, Equation V-5a, in logarithmic form

$$\ln \Theta_i = \ln (f^V/P)_P - \ln (f^L/p_i^o)_P \qquad (V\text{-}8)$$

Combining Equations V-6, V-7 and V-8 and rearranging

$$\ln \Theta_i = \frac{1}{RT}\int_{p_i^o}^{P} (V_i^V - \frac{RT}{P})\, dP - \frac{1}{RT}\int_{p_i^o}^{P} V_i^L\, dP \qquad (V\text{-}9)$$

The above equation is the general relationship for the imperfection pressure correction.

Two solutions to Equation V-9 are presented and discussed in Appendix F.

Imperfection Pressure Correction from Virial Coefficients

For the present consider the solution based on the volume-explicit Berlin virial equation of state

$$PV_i^V = RT + B_i'P + C_i'P^2 + D_i'P^3 + \ldots\ldots\ldots \qquad (V\text{-}10)$$

Substituting Equation V-10 into Equation V-9 and integrating gives the following expression for the imperfection pressure correction

$$\ln \Theta_i = \frac{1}{RT}\left[(B_i' - V_i^L)(P-p_i^o) + \frac{C_i'}{2}(P^2-p_i^{o2}) + \frac{D_i'}{3}(P^3-p_i^{o3}) + \ldots\ldots\ldots\right] \qquad (V\text{-}11)$$

The virial coefficients, B', C', D', etc., are to be distinguished from the analogous coefficients of the Leiden (density form) virial equation of state, which is

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots\ldots \qquad (V\text{-}12)$$

For an equivalent number of terms Equation V-12 gives a better fit to experimental data than Equation V-10. Equation V-10, how-

ever, is more convenient for this work. The quantities B and B' are called second virial coefficients; C and C', third virials; D and D', fourth virials, etc.

The relationships between the two sets of virial coefficients can be shown to be

$$B = B' \qquad \text{(V-13a)}$$

$$C' = \frac{C - B^2}{RT} \qquad \text{(V-13b)}$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^2} \qquad \text{(V-13-c)}$$

From the above equations it can be seen that each Berlin virial coefficient is related to the corresponding Leiden virial and all previous Leiden virial coefficients. These interrelationships have an important bearing on the selection of the equation for predicting the imperfection pressure correction.

For low pressures and approximations, a short form of Equation V-11 with C' and D' may be used. A plot of $\ln \Theta$ vs. pressure coordinates yields a straight line. At high pressures, this straight line relationship is not satisfactory. Additional virial coefficients are required.

Equation V-11 can be written in generalized form as follows

$$\ln \Theta = \frac{1}{T_r}\left(\frac{BP_c}{RT_c} - \frac{V^L P_c}{RT_c}\right)(P_r - p_r^o) + \frac{1}{2T_r}\left(\frac{C'P_c^2}{R\,T_c}\right)(P_r^2 - p_r^{o2})$$

$$+ \frac{1}{3T_r}\left(\frac{D'P_c^3}{R\,T_c}\right)(P_r^3 - p_r^{o3}) + \ldots\ldots \qquad \text{(V-14)}$$

Reduced vapor pressures are required when applying Equation

V-14. Several alternates were studied as routes to obtaining this quantity. These are discussed in Appendix D. The correlation finally chosen for this work is now summarized.

Pitzer et al. (51) correlated vapor pressure for reduced temperatures less than unity via the following equation

$$\ln p_r^o = (\ln p_r^o)^o + \omega \left(\frac{\partial \ln p_r^o}{\partial \omega} \right)_T \qquad \text{(V-15)}$$

where; $(\ln p_r^o)^o$ is the log of the vapor pressure of a simple fluid

$\left(\frac{\partial \ln p_r^o}{\partial \omega} \right)_T$ is the change of the vapor pressure with acentric factor

The correlation of Pitzer et al. (51) has been extrapolated to higher than unity reduced temperatures. Values of the terms in Equation V-15 for various T_r values are tabulated in Table XXII, Equations for computer solution for these coefficients and for the reduced vapor pressure are given in Appendix D.

The volume term in Equation V-14 is the generalized volume for the real and hypothetical liquid. The development of the correlation used for this term is discussed in Appendix C. The resulting correlation values are presented in Tables XX and XXI , These values are graphed in Figure 34 . The equations for computer application are presented in Appendix C,

The coefficients of the pressure difference terms in Equation V-14 may be written

$$\beta = \frac{1}{T_r} \left(\frac{BP_c}{RT_c} - \frac{V^L P_c}{RT_c} \right) \qquad \text{(V-16a)}$$

$$\frac{c'}{2} = \frac{1}{2T_r}\left(\frac{C'P_c^2}{RT_c}\right) = \frac{1}{2T_r}(c - b^2) \qquad \text{(V-16b)}$$

$$\frac{d'}{3} = \frac{1}{3T_r}\left(\frac{D'P_c^3}{RT_c}\right) = \frac{1}{3T_r}(d - 3bc + 2b^3) \qquad \text{(V-16c)}$$

where:

$$b = \frac{BP_c}{RT_c} = \text{generalized second virial coefficient} \qquad \text{(V-17a)}$$

$$c = \frac{CP_c^2}{R^2T_c^2} = \text{generalized third virial coefficient} \qquad \text{(V-17b)}$$

$$d = \frac{DP_c^3}{R^3T_c^3} = \text{generalized fourth virial coefficient} \qquad \text{(V-17c)}$$

Substitution of Equation V-16 into Equation V-14 yields the following

$$\ln \Theta = \beta(P_r - p_r^o) + \frac{c'}{2}(P_r^2 - p_r^{o2}) + \frac{d'}{3}(P_r^3 - p_r^{o3}) + \ldots \qquad \text{(V-18)}$$

Generalized equations for the second and third virial coefficients are required for the computation of the imperfection pressure correction. These virial coefficients may be evaluated from generalized equations of state by putting these equations in virial form. A review of some of the better known equations of state and their virial forms is given in Appendix B. Generalized equations for the second and third virial coefficients as a function of reduced temperature and acentric factor are also presented.

The imperfection pressure correction was evaluated for methane, propane and n-heptane at T_r=0.9 via the Redlich-Kwong (68), the Black (10), the Beattie-Bridgeman (3) and the Benedict-Webb-Rubin (7,9) equations of state. In addition, the imperfection pressure correction was evaluated using the Pitzer (62) generalized second virial equation with the third virial being determined from experimental data, and from the Pitzer second virial equation and the third virial equation developed in this work (Appendix E). Theta was also evaluated from fugacity coefficients via the K^o and K' values of Figures 6 and 7 as a tie-in to earlier work. Comparisons of values of the imperfection pressure correction from these different sources are given in Tables III through VI.

The new generalized equation for the third virial coefficient gives higher values for Θ than the Redlich-Kwong or the Beattie-Bridgeman equations. For propane and n-heptane the values of Θ predicted by the new equation are smaller than the values given by the R-K and B-B equations.

Comparisons of Θ values from two different sources are made in Tables VII through IX for methane, propane and n-heptane at different T_r and P_r values. These two sources of Θ values are: (1) values of Θ obtained from fugacity coefficients via the K^o and K' values of Figures 6 and 7, and (2) values of Θ calculated from the liquid volume and the generalized virial coefficients (Equation V-11). Vapor and system pressures are used in both computations.

The stepped dashed lines indicate the boundary between the

TABLE III

2ND AND 3RD VIRIAL COEFFICIENTS FOR METHANE AT $T_R = 0.9$ AND RESULTING IMPERFECTION PRESSURE CORRECTION VALUES

CASE		I	II	III	IV	V	VI	VII	VIII
B	CC/GMOL	-138.3	-125.2	-142.9	-141.8	--	-130.7	-138.3	--
C	CC/ATM GMOL	-2.866	-2.149	-1.864	-2.253	--	-2.359	-2.778	--
REDUCED PRESS.		IMPERFECTION PRESSURE CORRECTION VALUES							
0.50		1.0390	1.0352	1.0403	1.0399	1.0505	1.0380	1.0390	1.0311
0.60		0.9723	0.9760	0.9715	0.9717	0.9986	0.9730	0.9723	0.9649
0.80		0.8474	0.8619	0.8431	0.8449	0.8082	0.8480	0.8474	0.8285
1.00		0.7340	0.7590	0.7280	0.7300	0.7071	0.7360	0.7349	0.6817
2.00		0.3280	0.3860	0.3180	0.3218	0.3704	0.3240	0.3299	0.0448
3.00		0.1269	0.1680	0.1190	0.1221	0.2298	0.1200	0.1280	--
4.00		0.0424	0.0673	0.0381	0.0400	0.1798	0.0375	0.0429	--

SEE TABLE VI FOR LEGEND

TABLE IV

2ND AND 3RD VIRIAL COEFFICIENTS FOR PROPANE AT

T_R = 0.9 AND RESULTING IMPERFECTION PRESSURE

CORRECTION VALUES

CASE	I	II	III	IV	V	VI	VII	VIII
B CC/GMOL	-317.1	-280.9	-308.6	-299.3	--	-287.7	-317.1	--
C CC/ATM GMOL	-0.981	-0.713	-1.025	-1.002	--	-1.161	-0.963	--
REDUCED PRESS.	IMPERFECTION PRESSURE CORRECTION VALUES							
0.50	1.0020	1.0030	1.0020	1.0020	1.0000	1.0020	1.0030	1.0057
0.60	0.9336	0.9406	0.9381	0.9381	0.9000	0.9390	0.9390	0.9401
0.80	0.8049	0.8249	0.8165	0.8092	0.7600	0.8210	0.8060	0.8025
1.00	0.6881	0.7199	0.7101	0.7080	0.6700	0.7120	0.6900	0.5719
2.00	0.2841	0.3340	0.3282	0.3159	0.3500	0.3220	0.2860	0.0277
3.00	0.0965	0.1341	0.1319	0.1223	--	0.1240	0.0991	--
4.00	0.0274	0.0471	0.0471	0.0411	--	0.0410	0.0342	--

SEE TABLE VI FOR LEGEND

TABLE V

2ND AND 3RD VIRIAL COEFFICIENTS FOR HEPTANE AT

T_R = 0.9 AND RESULTING IMPERFECTION PRESSURE

CORRECTION VALUES

CASE	I	II	III	IV	V	VI	VII	VIII
B CC/GMOL	-778.2	-672.5	-722.3	-679.8	--	-693.3	-778.2	--
C CC/ATM GMOL	-10.79	-11.21	-6.009	-8.137	--	-9.192	-11.97	--
REDUCED PRESS.	IMPERFECTION PRESSURE CORRECTION VALUES							
0.50	0.9628	0.9664	0.9643	0.9674	0.9385	0.9666	0.9624	0.9732
0.60	0.8390	0.9032	0.8975	0.9066	0.8525	0.9038	0.8372	0.9078
0.80	0.7655	0.7845	0.7720	0.7920	0.7219	0.7862	0.7621	0.7659
1.00	0.6500	0.6750	0.6585	0.6885	0.6316	0.6800	0.6459	0.6039
2.00	0.2570	0.2835	0.2600	0.3118	0.3309	0.2960	0.2469	0.0112
3.00	0.0815	0.0970	0.0828	0.1220	--	0.1090	0.0750	--
4.00	0.0218	0.0270	0.0212	0.0420	--	0.0340	0.0186	--

SEE TABLE VI FOR LEGEND

TABLE VI

LEGEND FOR TABLES III, IV AND V

CASE I	PITZER ET AL. EQUATION FOR B PLUS MATTHEW AND HUND EXPERIMENTAL DATA FOR C (54)
CASE II	SU AND CHANG GENERALIZATION OF BEATTIE-BRIDGEMANN EQUATION (86)
CASE III	BENEDICT-WEBB-RUBIN EQUATION USING PUBLISHED CONSTANTS (7,9)
CASE IV	REDLICH AND KWONG EQUATION (68)
CASE V	EQUATION V-22 APPLIED WITH VAPOR PRESSURES PLUS K ZERO AND K PRIME FROM FIGURES 6 AND 7
CASE VI	BEATTIE-BRIDGEMANN EQUATION USING PUBLISHED CONSTANTS FOR METHANE, PROPANE OR HEPTANE (2)
CASE VII	GENERALIZED EQUATIONS FOR B AND C (EQUATIONS B-14, B-16, III-13b)
CASE VIII	CLINE BLACK EQUATION (10)

TABLE VII

COMPARISON OF IMPERFECTION PRESSURE CORRECTIONS

VIA EQUATIONS V-1 AND V-11

FOR METHANE (26)

P_r	Source of θ Values	Values of θ at indicated T_r					
		0.8	0.9	1.0	1.1	1.2	1.3
0.5	Eqn. V-1	0.7228	1.0505	1.282	1.719	1.748	1.938
	Eqn. V-11	0.8033	1.039	1.354	1.614	1.852	2.130
0.6	Eqn. V-1	0.6466	0.9986	1.204	1.572	1.707	1.926
	Eqn. V-11	0.7280	0.9723	1.272	1.554	1.797	2.080
0.8	Eqn. V-1	0.5089	0.8082	1.091	1.463	1.613	1.842
	Eqn. V-11	0.5908	0.8474	1.131	1.438	1.691	1.976
1.0	Eqn. V-1	*	0.7071	1.0	1.358	1.561	1.766
	Eqn. V-11	0.4740	0.7349	1.0	1.330	1.588	1.879
2.0	Eqn. V-1	*	0.370	0.6014	0.8889	1.150	1.435
	Eqn. V-11	0.1281	0.330	0.5160	0.8810	1.151	1.455
3.0	Eqn. V-1	*	*	*	0.6179	0.8591	1.113
	Eqn. V-11	0.0244	0.1280	0.2480	0.5560	0.8190	1.119
4.0	Eqn. V-1	*	*	*	0.4907	0.6797	0.9085
	Eqn. V-11	0.0032	0.0429	0.110	0.3480	0.5740	0.854

Note: Dashed line divides 'real' and 'hypothetical' states.

* - Beyond range of data for Equation V-1.

TABLE VIII

COMPARISON OF IMPERFECTION PRESSURE CORRECTIONS

VIA EQUATIONS V-1 AND V-11

FOR PROPANE (26)

P_r	Source of Θ Values	Values of Θ at indicated T_r					
		0.8	0.9	1.0	1.1	1.2	1.3
0.5	Eqn. V-1	0.6506	1.0000	1.282	1.717	1.943	2.2535
	Eqn. V-11	0.732	1.0000	1.348	1.820	2.545	3.5750
0.6	Eqn. V-1	0.5820	0.9000	1.204	1.590	1.897	2.239
	Eqn. V-11	0.7190	0.9272	1.274	1.745	2.465	3.475
0.8	Eqn. V-1	0.4580	0.7600	1.091	1.480	1.793	2.140
	Eqn. V-11	0.5030	0.7840	1.1325	1.600	2.308	3.300
1.0	Eqn. V-1	0.3824	0.6700	1.000	1.374	1.735	2.053
	Eqn. V-11	0.3800	0.6550	1.000	1.459	2.148	3.110
2.0	Eqn. V-1	*	0.3500	0.6013	0.8991	1.279	1.668
	Eqn. V-11	0.0678	0.2200	0.4825	0.8668	1.454	2.295
3.0	Eqn. V-1	*	*	*	0.6325	0.9548	1.2938
	Eqn. V-11	0.0058	0.058	0.1943	0.4635	0.9212	1.6200
4.0	Eqn. V-1	*	*	*	*	0.7555	1.0565
	Eqn. V-11	0.00028	0.0096	0.0660	0.2225	0.5460	1.0964

Note: Dashed line divides 'real' and 'hypothetical' states.

* - Beyond range of data for Equation V-1.

TABLE IX

COMPARISON OF IMPERFECTION PRESSURE CORRECTIONS

VIA EQUATIONS V-1 AND V-11

FOR N-HEPTANE (26)

P_r	Source of θ Values	Values of θ at indicated T_r					
		0.8	0.9	1.0	1.1	1.2	1.3
0.5	Eqn. V-1	0.6088	0.9385	1.2820	1.814	2.205	2.687
	Eqn. V-11	0.6875	0.9625	1.2925	1.700	2.250	2.760
0.6	Eqn. V-1	0.5446	0.8525	1.2040	1.707	2.153	2.669
	Eqn. V-11	0.6080	0.8921	1.2373	1.642	2.132	2.700
0.8	Eqn. V-1	0.4286	0.7220	1.0910	1.589	2.035	2.552
	Eqn. V-11	0.4670	0.7620	1.1142	1.526	2.075	2.595
1.0	Eqn. V-1	0.2557	0.6316	1.0000	1.441	1.968	2.448
	Eqn. V-11	0.3510	0.6455	1.0000	1.420	1.965	2.490
2.0	Eqn. V-1	*	0.3309	0.6013	0.9652	1.451	1.989
	Eqn. V-11	0.060	0.2460	0.5500	0.9644	1.484	2.022
3.0	Eqn. V-1	*	*	*	0.6790	1.083	1.543
	Eqn. V-11	0.0057	0.0752	0.2760	0.6322	1.104	1.637
4.0	Eqn. V-1	*	*	*	0.5328	0.857	1.260
	Eqn. V-11	0.0031	0.0186	0.1262	0.4000	0.810	1.322

Note: Dashed lined divide 'real' and 'hypothetical' states.

* - Beyond range of data for Equation V-1.

'real' and 'hypothetical' vapor or liquid phases for the pure components. In the area to the right and above the dashed lines 'real' vapor or 'hypothetical' liquid will occur. In like manner, in the area to the left and below the dashed lines 'real' liquid or 'hypothetical' vapor will occur. These hypothetical states were discussed in Chapter I.

A requirement imposed on the final K-ideal correlation is that it give reasonable results when applied to the regions of 'hypothetical' vapors and liquids. It was found that correlations based on the equations of state or the generalized virial coefficients did not sufficiently satisfy this criterion and also that they did not cover the total range of interest for pressure and temperature.

Semi-Empirical Correlation

Accordingly, a semi-empirical equation was chosen as a solution to the problem. The form of this equation is as follows

$$\ln \Theta = \beta(P_r - p_r^o) + \psi(P_r^2 - p_r^{o2}) \qquad \text{(V-19)}$$

where: β is evaluated by Equation V-16a

ψ is evaluated empirically as described below

Values of β were calculated from Equation V-16a using Equations B-17 and C-6. This generalized second virial coefficient is tabulated in Table X and presented graphically in Figure 18.

The generalized β coefficient can be written in the form

$$\beta = \beta^o + \omega\beta' \qquad \text{(V-20)}$$

TABLE X

GENERALIZED BETA COEFFICIENT FOR IMPERFECTION

PRESSURE CORRECTION EQUATION

REDUCED TEMP.	BETA COEFFICIENT AT ACENTRIC FACTOR = 0.0	0.10	0.20	0.30	0.40	0.50
.60	-1.57969	-1.81306	-2.04642	-2.27978	-2.51315	-2.74651
.65	-1.29026	-1.43667	-1.58308	-1.72949	-1.87589	-2.02230
.70	-1.07214	-1.16723	-1.26232	-1.35742	-1.45251	-1.54760
.75	-.90410	-.96686	-1.02962	-1.09238	-1.15514	-1.21790
.80	-.77218	-.81353	-.85489	-.89625	-.93760	-.97896
.8	-.66690	-.69356	-.72022	-.74687	-.77353	-.80019
.90	-.58169	-.59797	-.61425	-.63053	-.64681	-.66309
.95	-.51183	-.52063	-.52944	-.53824	-.54704	-.55584
1.00	-.45393	-.45726	-.46059	-.46392	-.46726	-.47059
1.05	-.40545	-.40474	-.40402	-.40331	-.40260	-.40189
1.10	-.36449	-.36077	-.35705	-.35332	-.34960	-.34587
1.15	-.32962	-.32364	-.31767	-.31169	-.30572	-.29975
1.20	-.29970	-.29204	-.28438	-.27673	-.26907	-.26141
1.25	-.27386	-.26495	-.25604	-.24713	-.23822	-.22931
1.30	-.25140	-.24157	-.23173	-.22190	-.21206	-.20223
1.35	-.23178	-.22127	-.21076	-.20025	-.18975	-.17924
1.40	-.21455	-.20356	-.19257	-.18158	-.17059	-.15960
1.45	-.19934	-.18802	-.17670	-.16538	-.15407	-.14275
1.50	-.18585	-.17432	-.16279	-.15127	-.13974	-.12821
1.55	-.17385	-.16220	-.15055	-.13890	-.12725	-.11560
1.60	-.16313	-.15143	-.13973	-.12804	-.11634	-.10464
1.65	-.15352	-.14182	-.13013	-.11844	-.10675	-.09506
1.70	-.14486	-.13323	-.12159	-.10995	-.09831	-.08667
1.75	-.13706	-.12550	-.11395	-.10239	-.09084	-.07928
1.80	-.12999	-.11855	-.10710	-.09566	-.08422	-.07277
1.85	-.12358	-.11226	-.10095	-.08964	-.07832	-.06701
1.90	-.11774	-.10657	-.09540	-.08424	-.07307	-.06190
1.95	-.11241	-.10140	-.09039	-.07938	-.06837	-.05736
2.00	-.10755	-.09670	-.08585	-.07501	-.06416	-.05332

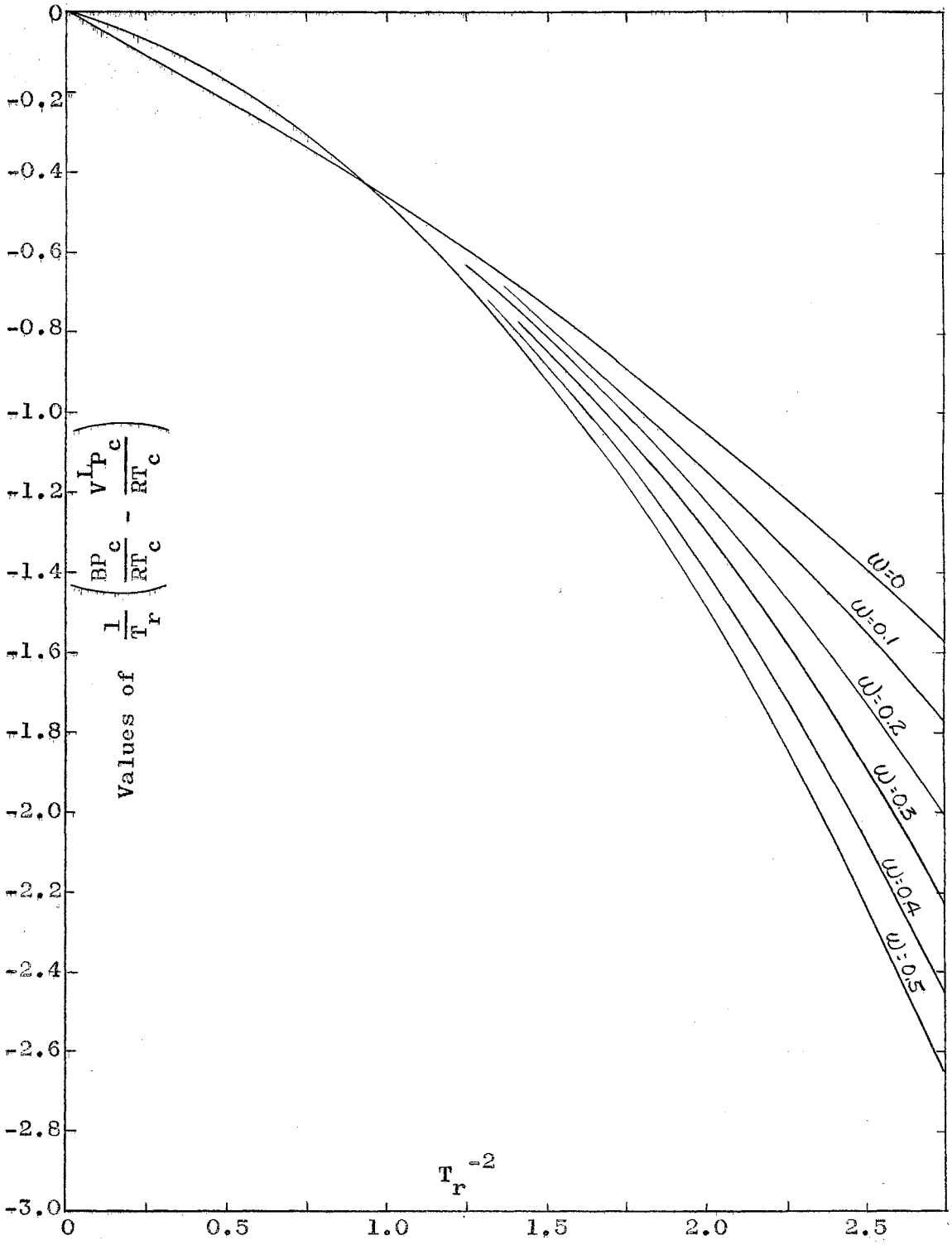

Figure 18

Generalized Coefficient of $(P_r - p_r^o)$ in Equation V-19 (23)

The terms β^o and β' are functions of reduced temperature only. β^o is the value for β for the simple fluid for which $\omega=0$. β' expresses the effect of the acentric factor on β. Values of β^o and β' are presented in Table XI. These values were obtained as follows

1. Values of β were calculated for each isotherm via Equation V-16a at acentric factors of zero and 0.5.
2. β^o is obtained directly as the value of β at $\omega=0$.
3. β' is obtained from the linear relationship between β and acentric factor

$$\beta' = \frac{\beta_{\omega=0.5} - \beta_{\omega=0.0}}{0.5} \qquad \text{(V-21)}$$

The above procedure is made possible by the fact that Equations B-17 and C-6 can be separated into two terms, one for the simple fluid and the other for the acentric factor correction.

A limited number of values of Θ were calculated via Equation V-19; the values of β used were those obtained above. The last term in the equation was assumed to be zero.

The ideal K-value can be expressed in terms of the imperfection pressure correction as follows

$$K_{Ideal} = \frac{p_i^o}{\Theta_i P} = \frac{\text{Vapor pressure}}{(\Theta)(\text{System Pressure})} \qquad \text{(V-22)}$$

Ideal K-values were calculated via Equation V-22 using Θ values based on β alone together with vapor pressures from Equation V-15. The resulting ideal K-values looked reasonable for the higher than unity reduced temperatures. At $T_r < 1.0$ the ideal K-values for $P_r \geq 1.0$ were obviously too high, the lower T_r curves

TABLE XI

GENERALIZED BETA COEFFICIENT FOR IMPERFECTION

PRESSURE CORRECTION EQUATION

EQUATION COEFFICIENTS

REDUCED TEMP.	SIMPLE FLUID BETA	BETA CHANGE WITH ACENTRIC FACTOR
.60	-1.57969	-2.33363
.65	-1.29026	-1.46407
.70	-1.07214	-.95092
.75	-.90410	-.62759
.80	-.77218	-.41357
.85	-.66690	-.26657
.90	-.58169	-.16280
.95	-.51183	-.08802
1.00	-.45393	-.03332
1.05	-.40545	.00712
1.10	-.36449	.03723
1.15	-.32962	.05974
1.20	-.29970	.07656
1.25	-.27386	.08908
1.30	-.25140	.09834
1.35	-.23178	.10508
1.40	-.21455	.10988
1.45	-.19934	.11317
1.50	-.18585	.11529
1.55	-.17385	.11649
1.60	-.16313	.11698
1.65	-.15352	.11690
1.70	-.14486	.11639
1.75	-.13706	.11554
1.80	-.12999	.11443
1.85	-.12358	.11313
1.90	-.11774	.11167
1.95	-.11241	.11010
2.00	-.10755	.10845

crossing the higher T_r curves.

This examination indicated that the last term in Equation V-19 cannot be neglected at the higher reduced pressures. An additional term or terms is necessary to give correct ideal K-values.

The generalized third virial coefficient, ψ, was next evaluated and correlated as a function of reduced temperature and acentric factor. The criterion used in evaluating this coefficient was one based on the convergence pressure concept discussed in Chapter II, i.e., values of ψ were found which made the reduced isotherms of K_{Ideal} converge at $K_{Ideal}=1.0$ at a particular value of reduced pressure.

Values of ψ were found which made the reduced ideal K-value isotherms converge at $K_{Ideal}=1.0$ at P_r values from 1 to 15. Values of ψ can be obtained by direct solution of the logarithmic form of Equation V-22 where Equation V-19 has been substituted for Θ. The resulting equation is

$$\psi = \frac{\ln p^o_{r_i} - \ln P_{r_k} - \beta(P_{r_k} - p^o_{r_i})}{(P^2_{r_k} - p^{o2}_{r_i})} \qquad (V\text{-}23)$$

Direct solution for ψ via Equation V-23 is possible for all reduced convergence pressures up to and including $P_{r_k}=6.29$. At $P_{r_k} > 6.29$ additional terms are required in Equation V-19 if the convergence criterion is to be satisfied.

An early thought was that ideal K-values could be determined in generalized form for a particular convergence pressure as is

done in the present NGSMA convergence pressure based K-value correlations (57). The ideal K-value for a component of a mixture would be determined as follows

1. Evaluate the convergence pressure in the conventional manner (57).
2. Find the reduced convergence pressure for the component as the ratio of the convergence pressure to the pure component critical pressure.
3. Evaluate β via Equation V-16a and ψ via Equation V-23.
4. Calculate Θ via Equation V-19.
5. Calculate the ideal K-value via Equation V-22.

A look at Figure 19 shows such a procedure is not adequate. Figure 19 presents the K-values for the methane-decane system at 280°F. as a function of pressure and as a function of reduced pressure. Note that the K vs. pressure curves converge at K=1.0 and 4600 psia while the K vs. reduced pressure curves for the individual components converge at K=1.0 and different reduced pressure values.

The above discussion points to the necessity of a common reduced convergence pressure for the ideal K-value correlation if convergence pressure is to be used as a correlating criterion.

The limiting value of $P_{r_k}=6.29$ for two constants in Equation V-19 was chosen as the basis for the imperfection pressure correction correlation. Values of ψ were determined via Equation V-23. These values are tabulated as a function of reduced temperature and acentric factor in Table XII and are graphed in Figure 20.

The generalized ψ coefficient can be written

$$\psi = \psi^{\circ} + \omega\psi' \qquad \text{(V-24)}$$

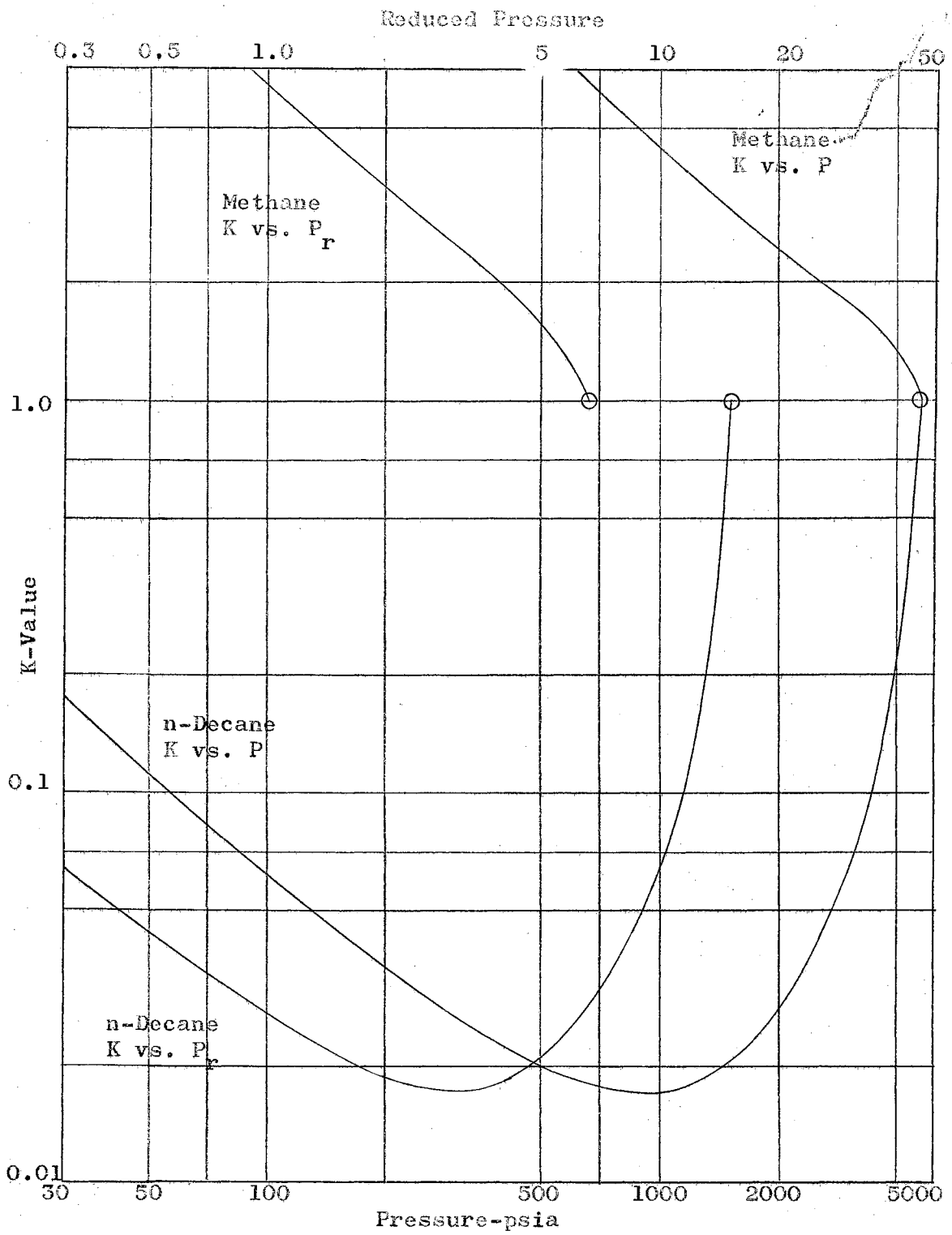

Figure 19

K-Values for Methane-n-Decane at 280°F.

Ind. Eng. Chem., Dec., 1942

TABLE XII

PSI AS A FUNCTION OF TR AND OMEGA

REDUCED TEMP.	PSI AT ACENTRIC FACTOR = 0.0	0.1	0.2	0.3	0.4	0.5
.60	.11327	.14073	.16814	.19552	.22286	.25017
.65	.08394	.09989	.11580	.13167	.14750	.16329
.70	.06326	.07290	.08252	.09209	.10163	.11113
.75	.04837	.05435	.06031	.06624	.07215	.07803
.80	.03744	.04120	.04495	.04868	.05240	.05610
.85	.02928	.03164	.03400	.03635	.03869	.04103
.90	.02309	.02455	.02601	.02746	.02892	.03038
.95	.01834	.01920	.02006	.02092	.02179	.02265
1.00	.01466	.01511	.01557	.01603	.01648	.01694
1.05	.01177	.01201	.01225	.01248	.01270	.01292
1.10	.00949	.00960	.00969	.00978	.00985	.00990
1.15	.00768	.00771	.00772	.00770	.00767	.00761
1.20	.00623	.00622	.00617	.00610	.00599	.00585
1.25	.00507	.00504	.00497	.00485	.00469	.00451
1.30	.00414	.00410	.00401	.00387	.00369	.00347
1.35	.00339	.00336	.00326	.00311	.00291	.00268
1.40	.00279	.00276	.00266	.00251	.00231	.00208
1.45	.00229	.00228	.00219	.00203	.00184	.00161
1.50	.00189	.00189	.00180	.00166	.00147	.00126
1.55	.00157	.00157	.00150	.00136	.00118	.00098
1.60	.00130	.00132	.00125	.00112	.00096	.00077
1.65	.00108	.00111	.00105	.00093	.00078	.00061
1.70	.00090	.00094	.00089	.00078	.00064	.00048
1.75	.00075	.00080	.00076	.00066	.00053	.00039
1.80	.00063	.00069	.00065	.00056	.00044	.00031
1.85	.00053	.00059	.00056	.00048	.00037	.00025
1.90	.00044	.00051	.00049	.00041	.00031	.00020
1.95	.00037	.00045	.00043	.00035	.00026	.00017
2.00	.00032	.00039	.00038	.00031	.00022	.00014

PSI = GREEK LETTER, ψ

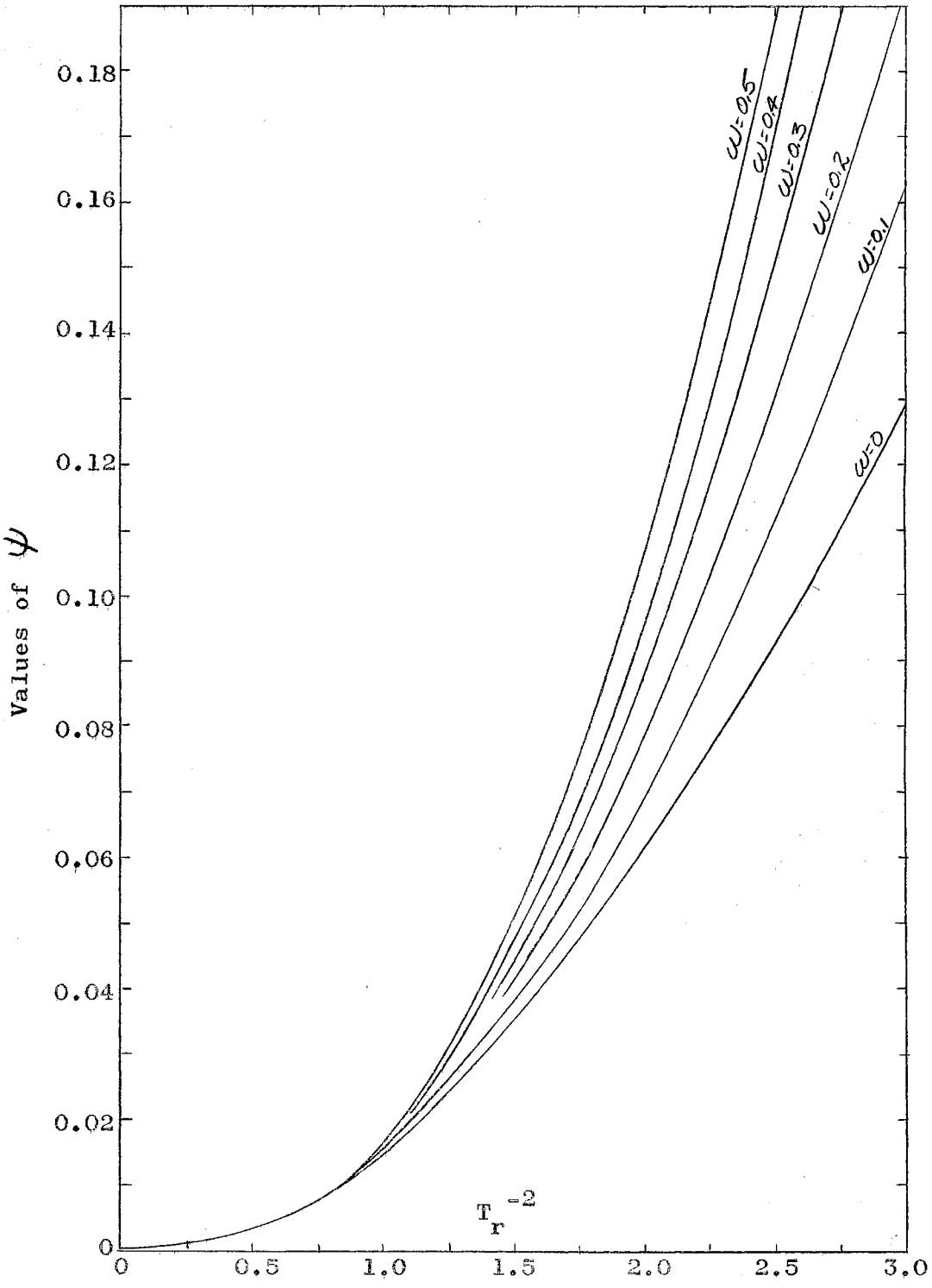

Figure 20

Generalized Coefficient of $(P_r^2 - p_r^{o2})$ in Equation for

Imperfection Pressure Correction

The terms ψ^{o} and ψ' are functions of reduced temperature only, ψ^{o} is the value for ψ for the simple fluid (ω=0). ψ' expresses the effect of acentric factor on ψ. Values of ψ^{o} and ψ' are presented in Table XIII. These values were obtained in the same manner as the β^{o} and β' values.

Values of ln Θ were calculated for several acentric factors using the values of β and ψ from Tables X and XII and Equation V-19. The resulting values were put in the form

$$\ln \Theta = \ln \Theta^{o} + \omega \ln \Theta' \qquad \text{(V-25)}$$

Figure 21 is a plot of ln Θ^{o}, the value of the imperfection pressure correction for the simple fluid, vs. reduced temperature and reduced pressure. Values of ln Θ' are presented in Figure 22 as a function of reduced temperature and reduced pressure.

Values of K^{o}_{Ideal} and K'_{Ideal} were computed from the following relationships

$$\ln K^{o} = (\ln p_r^{o})^{o} - \ln P_r - \ln \Theta^{o} \qquad \text{(V-26)}$$

$$\ln K' = \left(\frac{\partial \ln p_r^{o}}{\partial \omega} \right)_T - \ln \Theta' \qquad \text{(V-27)}$$

Values of K^{o}_{Ideal} from Equation V-26 are presented in Figure 23 as a function of reduced temperature and reduced pressure. Values of K'_{Ideal} from Equation V-27 are presented in Figure 24 as a function of reduced temperature and reduced pressure.

TABLE XIII

GENERALIZED PSI COEFFICIENT FOR IMPERFECTION

PRESSURE CORRECTION EQUATION

EQUATION COEFFICIENTS

REDUCED TEMP.	SIMPLE FLUID PSI	PSI CHANGE WITH ACENTRIC FACTOR
.60	.11327	.27398
.65	.08394	.15890
.70	.06326	.09592
.75	.04837	.05946
.80	.03744	.03739
.85	.02928	.02354
.90	.02309	.01457
.95	.01834	.00861
1.00	.01466	.00457
1.05	.01177	.00233
1.10	.00949	.00089
1.15	.00768	-.00002
1.20	.00623	-.00060
1.25	.00507	-.00094
1.30	.00414	-.00112
1.35	.00339	-.00119
1.40	.00279	-.00119
1.45	.00229	-.00113
1.50	.00189	-.00105
1.55	.00157	-.00095
1.60	.00130	-.00085
1.65	.00108	-.00075
1.70	.00090	-.00065
1.75	.00075	-.00056
1.80	.00063	-.00048
1.85	.00053	-.00040
1.90	.00044	-.00033
1.95	.00037	-.00028
2.00	.00032	-.00023

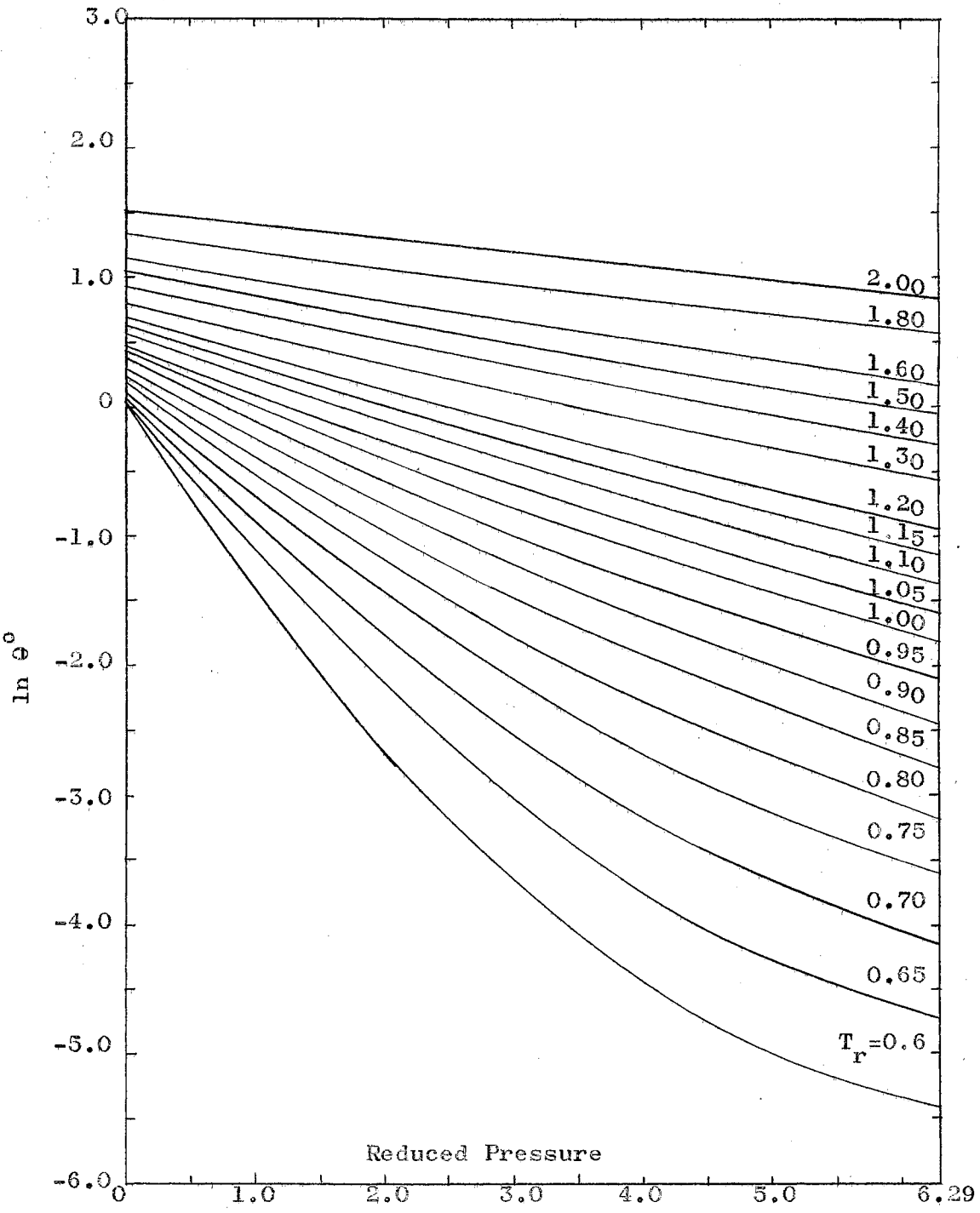

Figure 21

Imperfection Pressure Correction for Simple Fluid

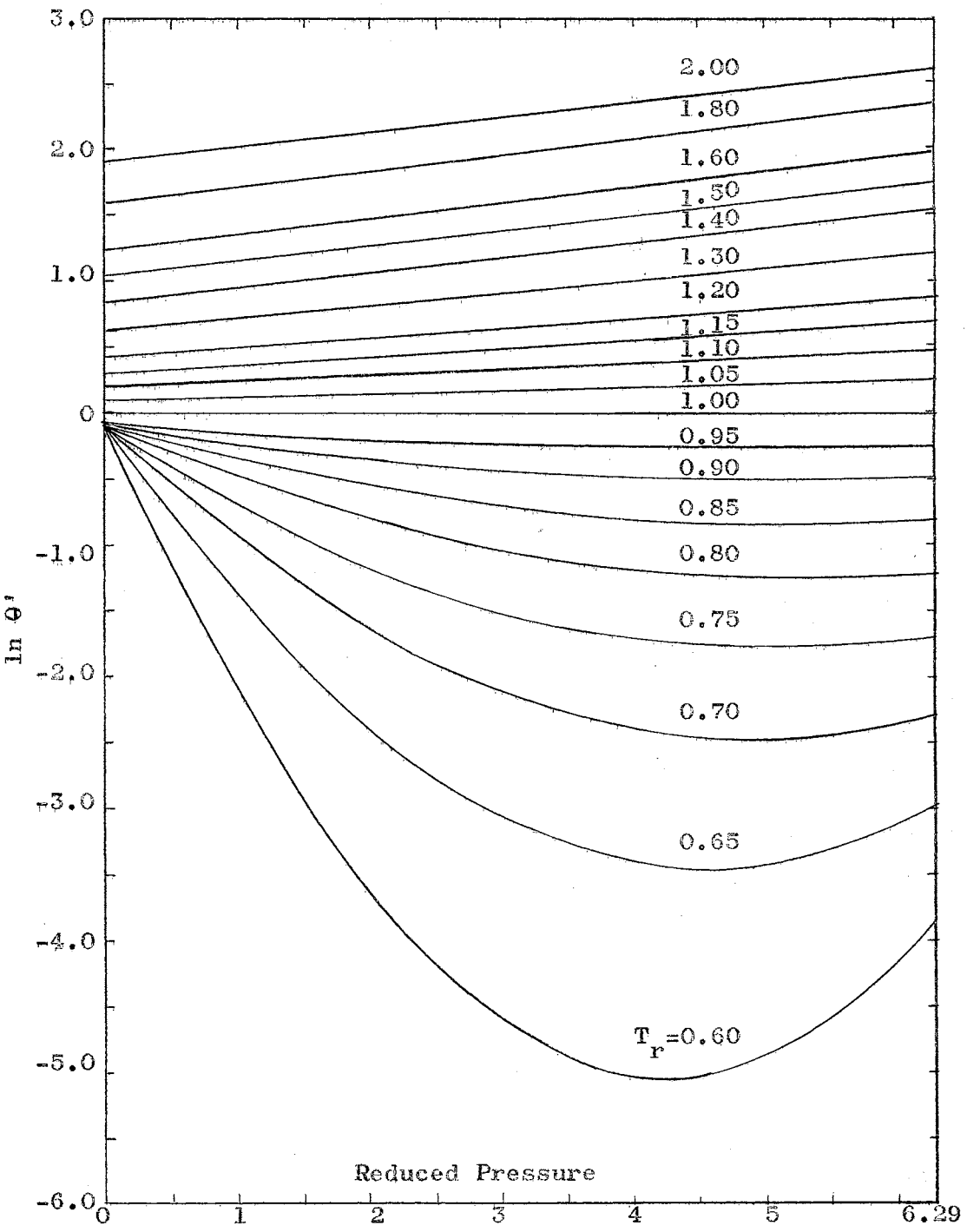

Figure 22

ln Θ' vs. T_r and P_r (P_{r_k}=6.29)

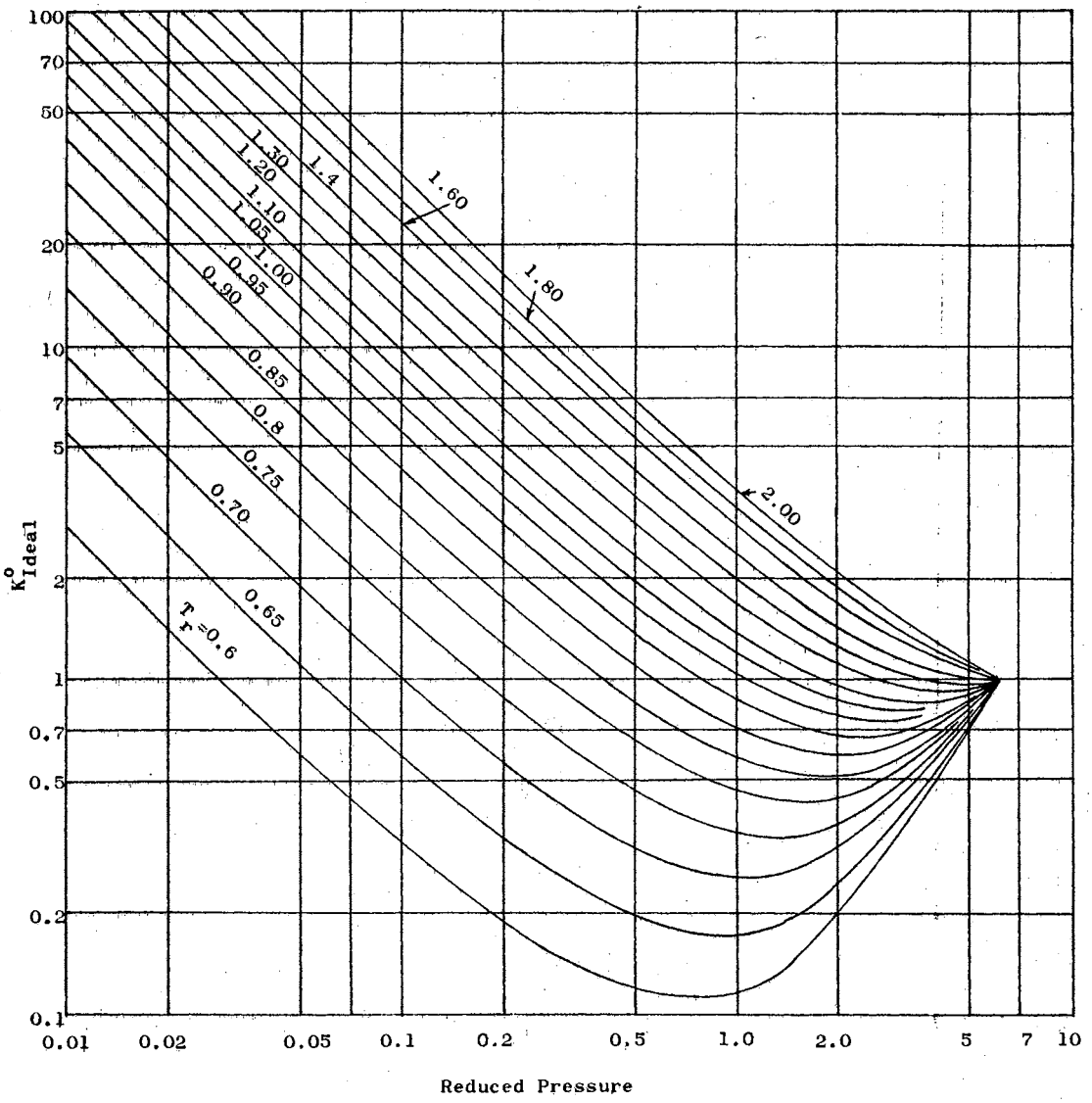

Figure 23

Ideal K-Value for Simple Fluid (P_{r_k}=6.29)

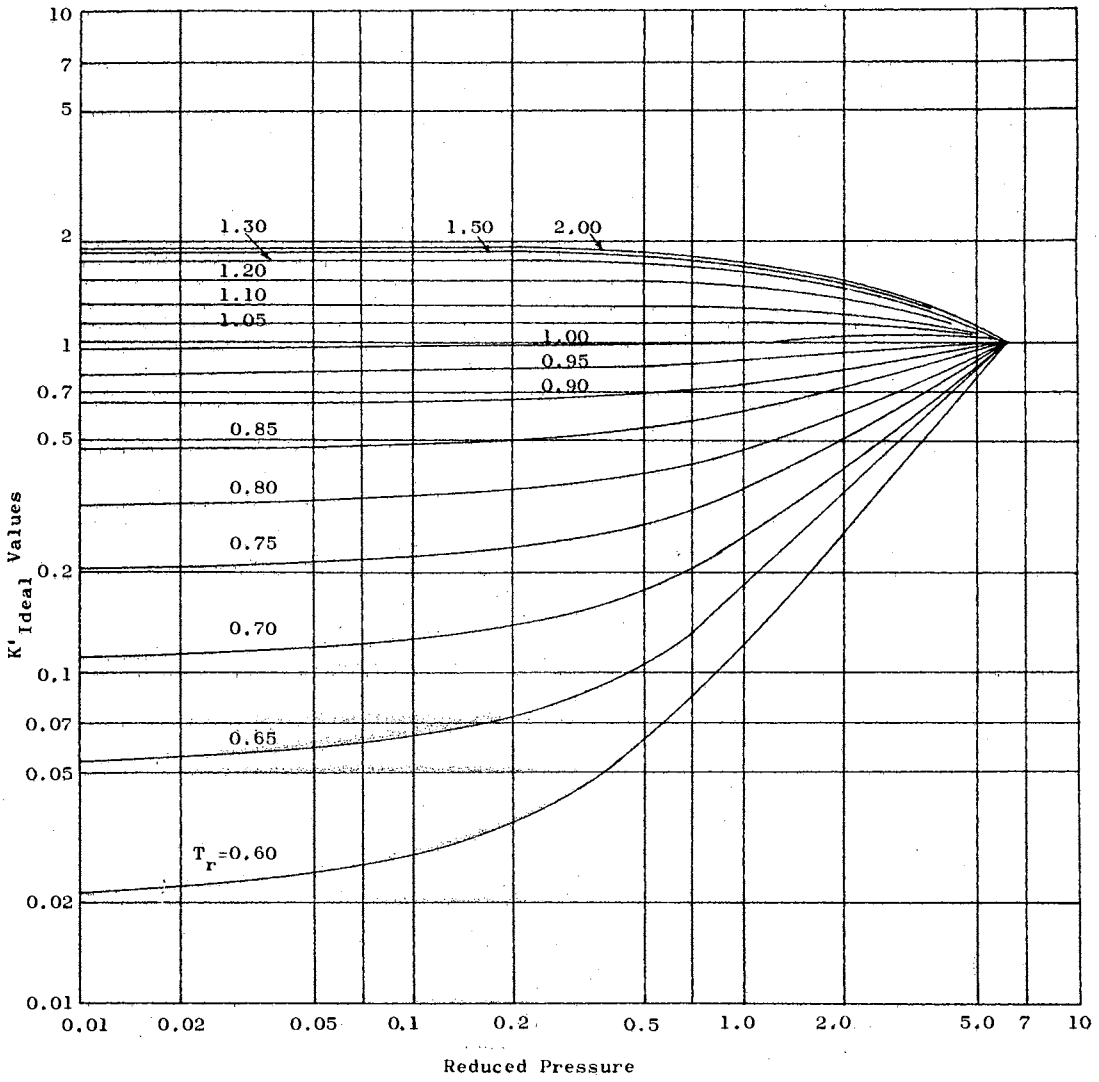

Figure 24

K' Ideal Values (P_{r_k}=6.29)

CHAPTER VI

ACTIVITY COEFFICIENTS

Activity coefficients are measures of the departure from ideal solutions. The activity coefficient is the ratio of two fugacity coefficients, i.e., the ratio of the fugacity coefficient of a component in a mixture to its fugacity coefficient as a pure component at the same temperature and pressure.

In terms of fugacities the activity coefficients are expressed symbolically

$$\gamma_i^L = \bar{f}_i^L / f_i^L x_i \qquad \text{(VI-1)}$$

$$\gamma_i^V = \bar{f}_i^V / f_i^V y_i \qquad \text{(VI-2)}$$

The fugacities are all at the system temperature and pressure and in the indicated phase. A bar above the fugacity indicates values of the fugacity in a mixture while no bar indicates the pure state, either vapor or liquid.

For ideal solutions where volumes are additive, i.e., obeying Amagat's Law:

$$\bar{f}_i^L = f_i^L x_i \qquad \text{(VI-3)}$$

and

$$\bar{f}_i^V = f_i^V x_i \qquad \text{(VI-4)}$$

Equations VI-3 and VI-4 are the well known Lewis and Randall

fugacity rule discussed in Chapter II. The activity coefficients approach unity as the mole fractions approach unity.

The activity coefficients for hydrocarbon systems are greater than unity and increase with decreasing concentration, reaching a maximum at infinite dilution. Activity coefficients are dependent on solute concentration as well as the character of the solute and the solvent.

Liquid Activity Coefficients

Hildebrand and Scott (34) and Scatchard (76,77) have shown that the activity coefficient, γ_i^L, of a component 'i' in a regular liquid solution containing n components is given by

$$\ln \gamma_i^L = \frac{V_i^L}{RT} (\delta_i - \bar{\delta})^2 \qquad \text{(VI-5)}$$

where: γ_i^L = the liquid activity coefficient of component 'i'

V_i^L = the molar liquid volume of component 'i'

δ_i = the solubility parameter of component 'i'

$\bar{\delta}$ = the liquid volume average solubility parameter for the entire mixture

$$\bar{\delta} = \frac{\sum x_i V_i \delta_i}{\sum x_i V_i} = \sum X_{V_i} \delta_i \qquad \text{(VI-6)}$$

$$X_{V_i} = \frac{x_i V_i}{\sum x_i V_i} \qquad \text{(VI-7)}$$

A similar equation may be written for every component of the mixture. For example

$$\ln \gamma_2^L = \frac{V_2^L}{RT} (\delta_2 - \bar{\delta})^2 \qquad \text{(VI-8)}$$

Pipkin (61) included an excellent discussion on the development of the above equations in his thesis on the correlation of equilibrium data for methane binaries through the use of solubility parameters. There is no need to repeat these derivations.

The Scatchard-Hildebrand equation for 'regular' solutions is a satisfactory relationship for predicting the liquid phase activity coefficient for the components of hydrocarbon mixtures even though the equation has limitations, i.e., it always yields activity coefficients greater than unity.

The following properties are generally accepted as defining 'regular' solutions: (1) the entropy of mixing is ideal, (2) the volume change on mixing is zero, (3) orienting and chemical effects are absent, and (4) pair additivity.

Not all solutions are 'regular'. A theoretical difficulty with the use of the Scatchard-Hildebrand equation is that the parameters (V and δ) for a gas in liquid solution must be hypothetical properties. However, the Scatchard- Hildebrand equation gives an excellent first approximation of the liquid activity coefficient.

For a binary mixture Equation VI-5 reduces to the following form

$$\ln \gamma_i^L = \frac{V_1^L}{RT} (\delta_1 - \delta_2)^2 X_{V_2}^2 \qquad \text{(VI-9)}$$

and

$$\ln \gamma_2^L = \frac{V_2^L}{RT} (\delta_1 - \delta_2)^2 X_{V_1}^2 \qquad \text{(VI-10)}$$

From Equations VI-9 and VI-10 the van-Laar equations are obtained for both components.

$$\ln \gamma_1^L = \frac{A}{\left[\frac{x_1}{x_2}\,\frac{A}{B} + 1\right]^2} \qquad \text{(VI-11)}$$

$$\ln \gamma_2^L = \frac{B}{\left[\frac{x_2}{x_1}\,\frac{B}{A} + 1\right]^2} \qquad \text{(VI-12)}$$

where;

$$A = \frac{V_1^L}{RT}(\delta_1-\delta_2)^2 \qquad \text{(VI-13)}$$

$$B = \frac{V_2^L}{RT}(\delta_1-\delta_2)^2 \qquad \text{(VI-14)}$$

Equations VI-9 through VI-12 are more convenient for calculations for binary systems, however, they can be applied to multicomponent mixtures by considering component two as a hypothetical component that is a mixture of all the components in the mixture except component one. In this case V_2^L will be a molar volume average of all components in the hypothetical component two. Similarly, the value of δ_2 will be the liquid volume average of the δ values for all components in the hypothetical component two. Identical results are obtained for multicomponent mixtures by applying Equation VI-5 or Equations VI-9 through VI-12. The author has found Equation VI-5 to be the preferred form for computer application.

Pigg (60),working with ethane binaries, and Pipkin (61) working with methane binaries, demonstrated that a single value of the solubility parameter (i.e., independent of temperature) could be used in applying the Scatchard-Hildebrand equation for the liquid

activity coefficient. Chao and Seader (15) also used a single value of the solubility parameter in their correlation. The solubility parameter value chosen is the value at 25°C. Hildebrand and Scott (34) have tabulated values of the solubility parameter for many substances. Where values of the solubility parameter are not tabulated in the literature, a procedure outlined in Appendix H may be used for solubility parameter estimation. Values of the solubility parameter for various substances have been tabulated in Table XXVII.

Chao and Seader (15) used a single value for the molar liquid volume which was independent of temperature. Pipkin (61) found that the volumes obtained from the Watson liquid volume expression (Equation C-1) gave better results than the constant volume values used by Chao and Seader. The equations of Appendix C are recommended for evaluating liquid volumes.

A graphical solution of the Scatchard-Hildebrand equation in the form of a nomograph was prepared with the assistance of S.F. Chung. Nomographs covering two different ranges of values of the liquid activity coefficient are presented in Figures 43 and 44 . The procedure for applying these nomographs is outlined in Appendix I.

Vapor Activity Coefficients

Vapor activity coefficients can be determined in two ways, namely, (1) from the equilibrium vapor composition data using the calculation method discussed in Chapter IV and (2) from experimental data and ideal K-values using the Scatchard-Hildebrand

liquid activity coefficients in a back-calculation scheme. The first method was applied to the experimental data of three binaries at three different isotherms each (Chapter IV). This method is slow and tedious and is limited to low and moderate pressures.

Theoretically, the vapor activity coefficient may be computed by integrating the difference between partial and pure volumes as follows

$$\ln \gamma_i^V = \frac{1}{RT} \int_0^P (\bar{V}_i^V - V_i^V)\, dP \qquad \text{(VI-15)}$$

The difficulty involved in calculating vapor activity coefficients via Equation VI-15 is the evaluation of the volume difference term $(\bar{V}_i^V - V_i^V)$.

Partial volumes can be determined from experimental PVTX data for mixtures. The pure vapor state values can be determined in cases where the component can exist as a pure gas. In some cases the pure component volume term would be the molar volume for a hypothetical vapor.

A look at the volumetric behavior of a mixture indicates the form of the volume difference term.

The excess volume for a binary mixture is defined as

$$V^E = y_1 (\bar{V}_1 - V_1) + y_2 (\bar{V}_2 - V_2) \qquad \text{(VI-16)}$$

Defining a new term

$$\Delta V_i = \bar{V}_i - V_i \qquad \text{(VI-17)}$$

then Equation VI-16 becomes

$$V^E = y_1 \Delta V_1 + y_2 \Delta V_2 \qquad \text{(VI-18)}$$

where: $\Delta V_i = \overline{V}^E$ = the partial excess volume at infinite dilution

The simplest possible relationship for $\overline{V}_i^E$ is a straight line function of vapor mole fraction. Figure 25 is a plot of $\overline{V}_i^E$ vs. mole fraction in the vapor made with the assumption of the straight line relationship mentioned above. The lines on Figure 25 were drawn arbitrarily. They could have been drawn with ΔV negative or with the slope of the ΔV_1 curve greater than the slope of the ΔV_2 curve.

An examination of Figure 25 indicates the form of the ΔV relationships

$$\Delta V_1 \longrightarrow 0 \quad \text{as} \quad y_1 \longrightarrow 1.0 \qquad \text{(VI-19)}$$

$$\Delta V_2 \longrightarrow 0 \quad \text{as} \quad y_2 \longrightarrow 1.0 \qquad \text{(VI-20)}$$

The relationships of Figure 25 are represented symbolically

$$\overline{V}_1^E = \Delta V_1 = \overline{V}_{\infty 1}^E (1-y_1) \qquad \text{(VI-21)}$$

$$\overline{V}_2^E = \Delta V_2 = \overline{V}_{\infty 2}^E (1-y_2) \qquad \text{(VI-22)}$$

$\overline{V}_{\infty 1}^E$ and $\overline{V}_{\infty 2}^E$ are some functions or constants to be determined. $\overline{V}_{\infty 1}^E$ and $\overline{V}_{\infty 2}^E$ have the dimensions of volume. They are the partial excess volumes at infinite dilution.

Table XIV presents a summary of the calculations of the excess volumes for Figure 26 from the ΔV values of Figure 25. These calculations are included to illustrate the relationship between the excess volume and the $(\overline{V}-V)$ difference. The straight line

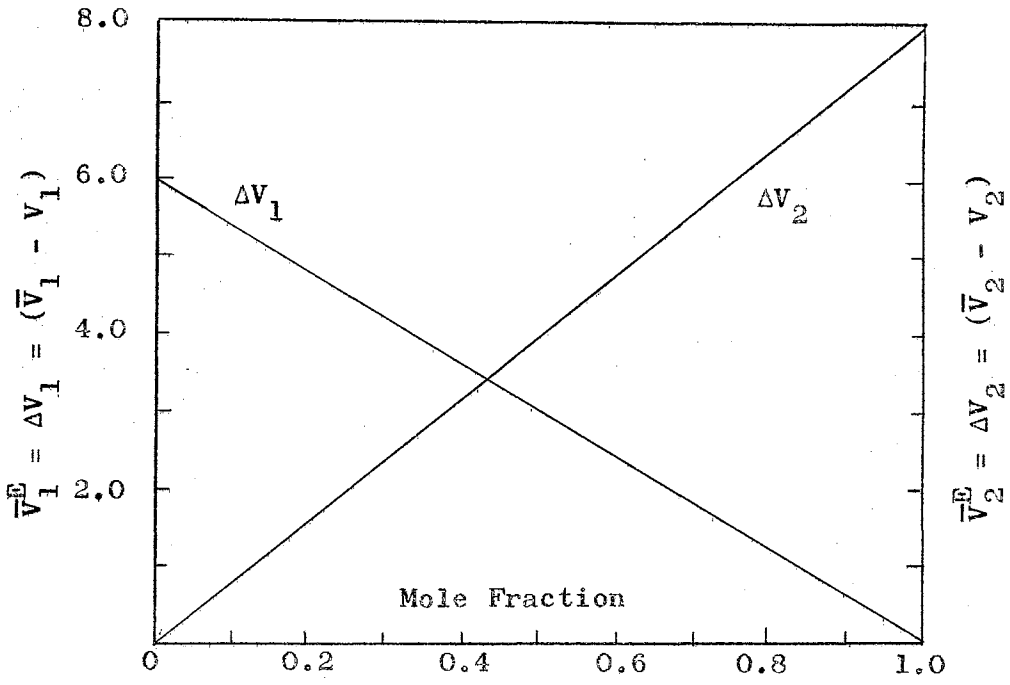

Figure 25

Straight Line ΔV Relationships for

Excess Volume Calculations (25)

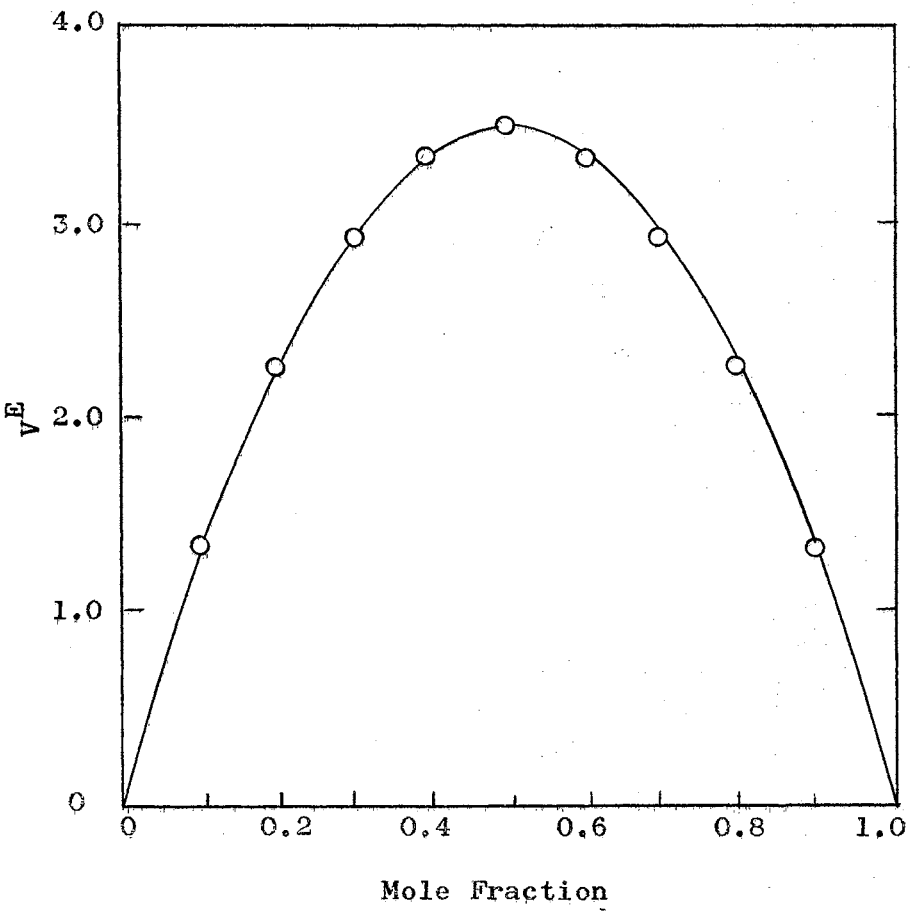

Figure 26

Excess Volume vs. Composition for

Straight Line ΔV Relationship (25)

TABLE XIV

CCALCULATIONS OF EXCESS VOLUMES FOR

FIGURE 26 FROM ΔV IN FIGURE 25 (25)

y_1	ΔV_1	$y_1 \Delta V_1$	ΔV_2	$y_2 \Delta V_2$	V^E
0	6.0	0	0	0	0
0.1	5.4	0.54	0.8	0.72	1.36
0.2	4.8	0.96	1.6	1.28	2.24
0.3	4.2	1.26	2.4	1.68	2.94
0.4	3.6	1.44	3.2	1.92	3.36
0.5	3.0	1.50	4.0	2.00	3.50
0.6	2.4	1.44	4.8	1.92	3.36
0.7	1.8	1.26	5.6	1.68	2.94
0.8	1.2	0.96	6.4	1.28	2.24
0.9	0.6	0.54	7.2	0.72	1.36
1.0	0	0	8.0	0	0

relationship for $\bar{V}_i^E$ in Figure 25 leads to the curved relationship for V^E in Figure 26.

Substituting Equation VI-21 into Equation VI-15, neglecting the effect of pressure on $\bar{V}_i^E$, and integrating gives

$$\ln \gamma_1^V = \frac{P\bar{V}_{\infty 1}^E}{RT} (1 - y_1) \qquad \text{(VI-23)}$$

A similar equation follows for component two.

Two assumptions have been made in deriving the above equation. The first assumption is the linear relation for $\bar{V}_i^E$, i.e., a straight line relationship between $\bar{V}_i^E$ and mole fraction. If Equations VI-21 and VI-22 are substituted into Equation VI-16, then

$$V^E = y_1 y_2 (\bar{V}_{\infty 1}^E + \bar{V}_{\infty 2}^E) \qquad \text{(VI-24)}$$

or

$$\frac{V^E}{y_1(1 - y_1)} = \bar{V}_{\infty 1}^E + \bar{V}_{\infty 2}^E \qquad \text{(VI-25)}$$

This implies that $V^E/y_1(1-y_1)$ is a constant. Beenakker and Coremans (5) have shown that $V^E/y_1(1-y_1)$ is essentially a constant at constant temperature and pressure for mixtures of nitrogen and hydrogen, but decreases slowly as pressure is increased.

The second assumption is that $\bar{V}^E$ is a constant at constant temperature and varying pressure. This assumption may or may not be valid. This assumption simplifies the correlation scheme and should be kept in mind when correlating vapor activity coefficients.

Vapor Activity Coefficients from Experimental Data

The vapor activity coefficients obtained from experimental y/x data in Chapter IV were used to calculate the values presented in Figures 27, 28, and 29. Figure 27 is a plot of ln $\gamma^V/(1-y)$ vs. P_r for the components of the ethane-n-heptane system. As can be seen from Equation VI-23 this ratio is equivalent to $P\bar{V}^E_\infty/RT$, which is a partial excess compressibility factor at infinite dilution.

Figure 28 is a plot of RT ln γ^V/P as a function of mole fraction ethane in the vapor phase. This ratio is equivalent to $\bar{V}^E_i$, provided the latter is not dependent on pressure. Straight lines would have been the result on Figure 28 if $\bar{V}^E_i$ had been constant. The plot shows the curvature that results in variable values of $\bar{V}^E_i$ as shown on Figure 29.

Each point on Figure 29 is obtained by extrapolation to zero of a line such as the dotted line in Figure 28. Figures 28 and 29 do not verify the simple correlating form proposed for vapor activity coefficients.

Values of $\bar{V}^E_\infty$ were evaluated from the experimental data for the ethane-n-butane and ethane-n-heptane binaries used in Chapter IV using the following equations

$$\gamma^V_i = \frac{K_{Ideal}}{K_{Actual}} \gamma^L_i = \frac{K^o(K')^\omega}{y/x} \gamma^L_i \qquad \text{(VI-26)}$$

$$\bar{V}^E_{\infty i} = \frac{RT \ln \gamma^V_i}{P(1-y)} \qquad \text{(VI-27)}$$

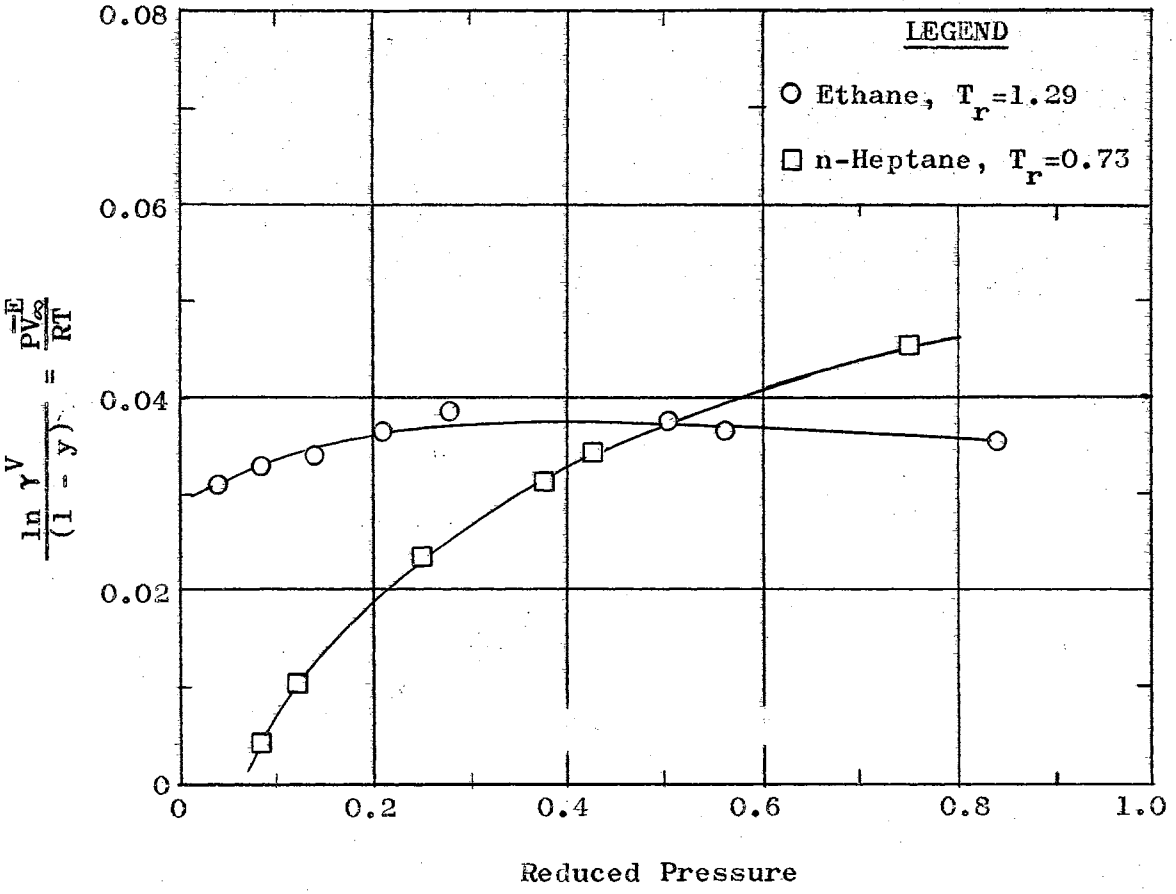

Figure 27

Partial Excess Compressibility Factors at Infinite Dilution for Ethane and n-Heptane System (23)

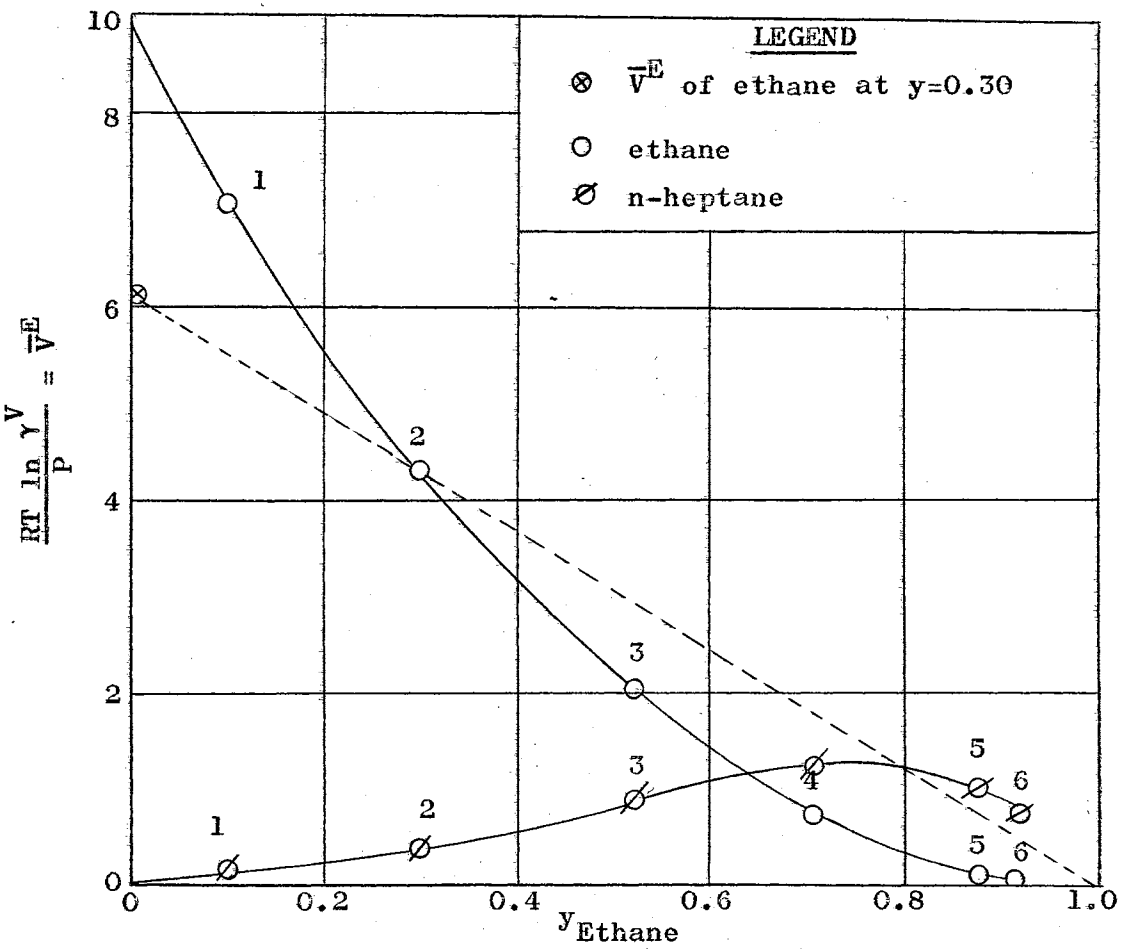

Figure 28

Partial Excess Volume for Ethane and Heptane at 250°F. (23)

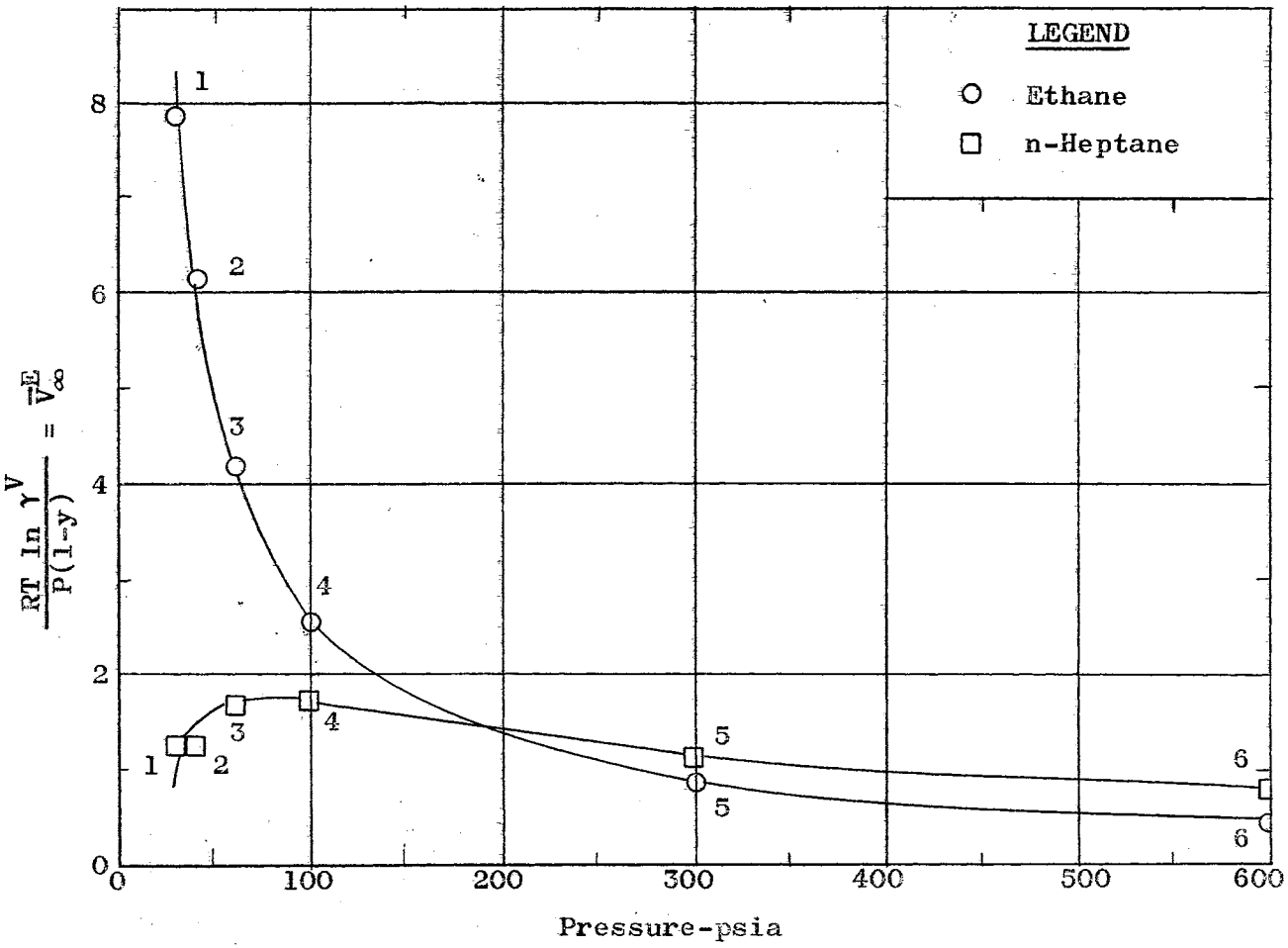

Figure 29

Partial Excess Volume at Infinite Dilution for Ethane and n-Heptane at 250°F. (23)

where: K^0 and K' are obtained from Figures 23 and 24.

γ_i^L is obtained from the Scatchard-Hildebrand equation.

y/x is obtained from experimental data.

Equation VI-27 is a rearrangement of Equation VI-23. The values of $\bar{V}_\infty^E$ for ethane in butane solvent and ethane in n-heptane solvent are presented in Figure 30 as a function of reciprocal reduced temperature. $\bar{V}_\infty^E$ is plotted on a logarithmic scale only as a convenience. It should be kept in mind that $\bar{V}_\infty^E$, evaluated by Equation VI-27, will be negative when the vapor activity coefficient is less than unity. When $\bar{V}_\infty^E$ is both positive and negative, a logarithmic scale cannot be used.

Equation VI-27 expresses $\bar{V}_\infty^E$ for the solute as a function of the pressure, temperature and concentration of the solvent. In the development of Equation VI-27 it was assumed that the pressure effect on $\bar{V}_\infty^E$ is only that shown in the equation.

Some qualitative observations concerning the use of Equation VI-27 have been made:

1. The effect of temperature on $\bar{V}_\infty^E$ cannot be neglected.
2. $\bar{V}_\infty^E$ was assumed to be a linear function of composition in the development of Equation VI-27. This assumption is not valid.
3. As temperature increases, solutions become more ideal. We, therefore, expect the vapor activity coefficient to approach unity and the partial excess volume at infinite dilution to approach zero as temperature is increased. Figure 30 supports this expectation.
4. In general, the results plotted in Figure 30 do not

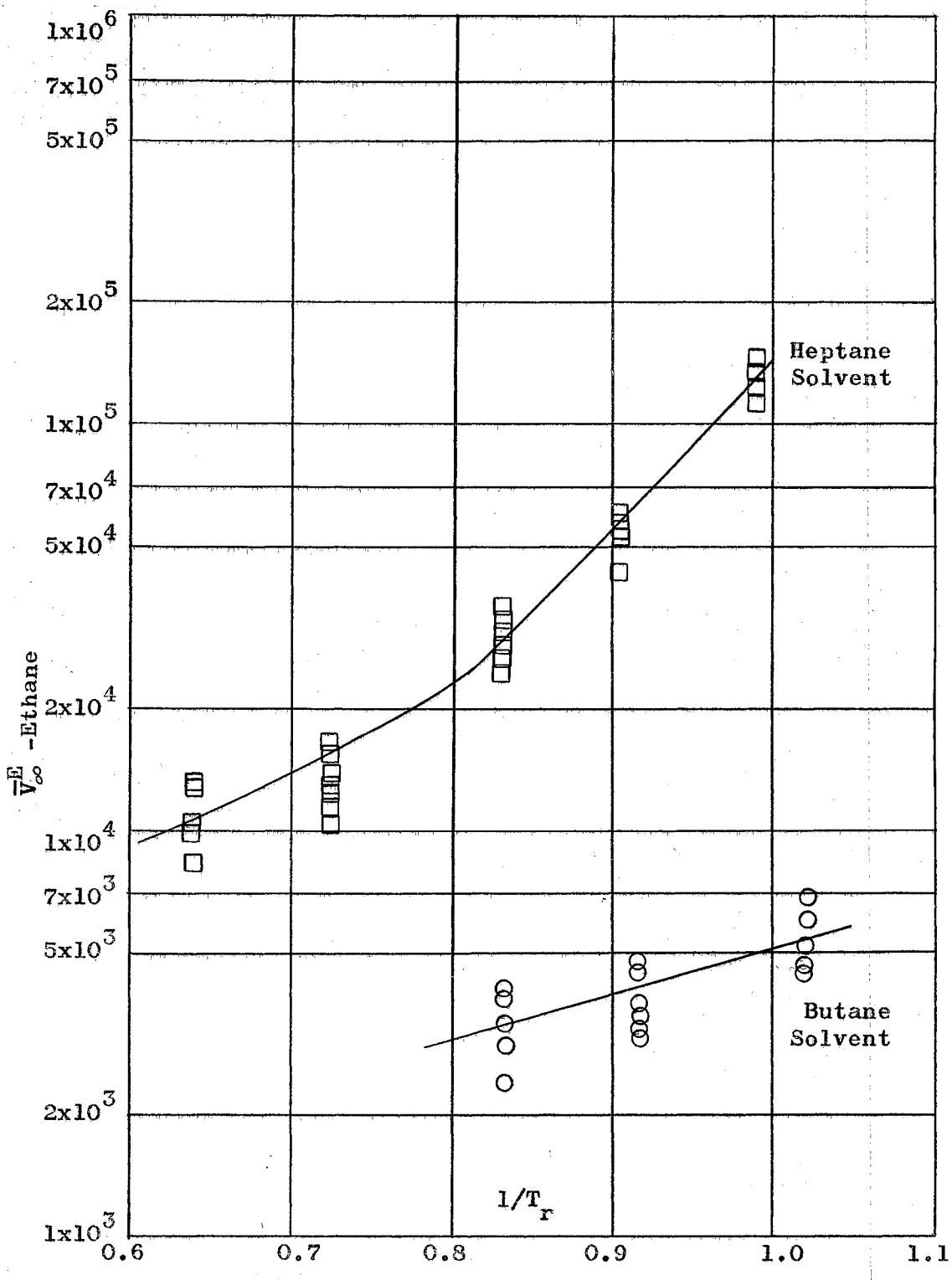

Figure 30

Partial Excess Volume at Infinite Dilution-Ethane Solute

verify the proposed correlating relationship (Equation VI-23). There is an effect of solvent or solute character which has not been properly accounted for in the correlating equation.

CHAPTER VII

RESULTS, CONCLUSIONS AND RECOMMENDATIONS

Results

The primary goal of this work has been to develop generalized ideal K-values that are suitable for the overall K-value correlation scheme

$$K = K_{Ideal} \frac{\gamma^L}{\gamma^V} \qquad \text{(VII-1)}$$

Values of K_{Ideal} for the simple fluid from various sources are compared in Table XV. These sources are: (1) the Hougen, et al. (41) K-values for the simple fluid (Figure 9), (2) ideal K-values based on the fugacity coefficients of Pitzer (51), Prausnitz (66) and Chao and Seader (15) which were revised to give unity K-values at the vapor pressures (Figure 6), (3) ideal K-values derived from x-y data by the calculation method discussed in Chapter IV (Figure 13) and (4) ideal K-values based on generalized vapor pressures and the imperfection pressure correction (Figure 23).

Figures 13 and 23 are in good agreement at the low reduced temperatures. The correlation based on fugacity coefficients (Figure 6) does not agree with any of the other correlations. This is partially explained by the low values of the f/P ratio for

TABLE XV

COMPARISON OF IDEAL K-VALUES FOR SIMPLE FLUID

T_r	P_r	Source of K^o Values: Figure 6 Modified f/P Values	Figure 9 Hougen Values	Figure 13 Ideal Fugacities	Figure 23 Imperfection Pressure Correction
0.65	0.10	0.65	0.01	0.60	0.25
	0.20	0.48	0.34	0.34	0.33
	0.50	0.44	0.21	0.22	0.19
	1.00	0.47	0.20	0.19	0.17
	2.00	0.60	0.21	----	0.25
0.70	0.10	1.00	1.05	1.00	1.00
	0.20	0.65	0.59	0.56	0.56
	0.50	0.52	0.34	0.33	0.30
	1.00	0.54	0.29	0.29	0.25
	2.00	0.64	0.30	----	0.30
0.80	0.10	2.15	2.20	----	2.30
	0.20	1.20	1.21	1.25	1.25
	0.50	0.74	0.66	0.65	0.63
	1.00	0.65	0.53	0.52	0.44
	2.00	0.69	0.53	----	0.43
0.90	0.10	3.70	4.05	----	4.20
	0.20	1.95	2.20	----	2.25
	0.50	1.04	1.04	----	1.04
	1.00	0.81	0.78	----	0.70
	2.00	0.75	0.74	----	0.59
1.0	0.10	6.20	6.10	----	6.70
	0.20	3.30	3.20	----	3.50
	0.50	1.55	1.50	----	1.60
	1.00	1.00	1.00	----	1.00
	2.00	0.81	0.92	----	0.76
1.20	0.10	13.70	12.50	----	12.20
	0.20	6.80	6.40	----	6.50
	0.50	2.85	2.75	----	2.80
	1.00	1.59	1.55	----	1.65
	2.00	1.10	1.10	----	1.09
1.40	0.10	26.00	21.00	----	18.50
	0.20	12.00	11.00	----	9.50
	0.50	4.70	4.60	----	4.00
	1.00	2.50	2.50	----	2.30
	2.00	1.45	1.55	----	1.40

the hypothetical vapor. The f/P values for the hypothetical vapor are discussed in Chapter III.

The Hougen correlation and the correlation based on the imperfection pressure correction are in fair agreement at the lower reduced temperatures, $T_r \leq 1.4$. There is a large difference between the two correlations at the higher reduced temperatures.

The preferred correlation is that based on the imperfection pressure correction, primarily due to the range of temperature and pressure covered. As pointed out this correlation is in good agreement with Figures 9 and 13 in the lower temperature range, the range in which correlation accuracy is hard to achieve.

Values of K'_{Ideal} from various sources are compared in Table XVI. The sources compared are: (1) values based on fugacity coefficients and the requirement that K=1.0 at the vapor pressure (Figure 7), (2) ideal K-values derived from x-y data by the calculation method of Chapter IV (Figure 17) and (3) ideal K-values based on the imperfection pressure correction (Figure 24).

The values of K' from Figure 17 indicate a reverse effect of pressure than that found on Figure 24. The development of Figure 7 indicated that K' was a function of reduced temperature only. The K' values via the imperfection pressure correction show only a slight effect of pressure at the lower reduced pressures for $T_I > 1.0$. The values of K' from Figure 24 bracket the constant K' value of Figure 7 at the lower reduced temperatures. The correlation based on the imperfection pressure correction indicates that there is a definite effect of pressure on K'.

TABLE XVI

COMPARISON OF K' VALUES

T_r	P_r	Source of K' Values: Figure 7 Modified f/P Values	Figure 17 Ideal Fugacities	Figure 24 Imperfection Pressure Correction
0.65	0.10	0.085	0.39	0.062
	0.20	0.085	0.57	0.072
	0.50	0.085	0.69	0.107
	1.00	0.085	0.72	0.198
	2.00	0.085	----	0.533
0.70	0.10	0.143	0.27	0.123
	0.20	0.143	0.45	0.135
	0.50	0.143	0.61	0.176
	1.00	0.143	0.63	0.264
	2.00	0.143	----	0.513
0.80	0.10	0.386	----	0.339
	0.20	0.386	0.35	0.353
	0.50	0.386	0.56	0.397
	1.00	0.386	0.58	0.474
	2.00	0.386	----	0.641
0.90	0.10	0.691	----	0.649
	0.20	0.691	----	0.660
	0.50	0.691	----	0.691
	1.00	0.691	----	0.741
	2.00	0.691	----	0.835
1.00	0.10	1.00	----	0.973
	0.20	1.00	----	0.978
	0.50	1.00	----	0.987
	1.00	1.00	----	1.000
	2.00	1.00	----	1.000
1.20	0.10	1.191	----	1.564
	0.20	1.191	----	1.556
	0.50	1.191	----	1.521
	1.00	1.191	----	1.465
	2.00	1.191	----	1.359
1.40	0.10	1.395	----	1.893
	0.20	1.395	----	1.863
	0.50	1.395	----	1.803
	1.00	1.395	----	1.708
	2.00	1.395	----	1.536

Conclusions

The major points from this study may be summarized as follows:

1. Ideal K-values based on generalized f/P correlations are limited in range of application and are not adequate for the lower reduced temperature and higher reduced pressure regions.
2. The modified Hoffman, Weber, et al. prccedure (Chapter IV) for evaluating standard state fugacities of hypothetical vapors from vapor activity coefficients is a useful method for obtaining ideal K-values. Application of this procedure is limited to systems where x-y data are available for the entire composition range. This limitation is circumvented by use of the van Laar equation for γ^V. The procedure of Chapter IV is further limited to the range of temperatures and pressures of the experimental vapor-liquid equilibrium data.
3. The imperfection pressure correction is the recommended basis for evaluating ideal K-values. The correlation presented in Figures 23 and 24 is applicable in its present form at $T_r \geq 1.0$ for all reduced pressures and at $P_r \leq 2.0$ for T_r 1.0. Convergence pressure should be discarded as a parameter of the K_{Ideal} correlation due to difficulties involved in definingthe convergence pressure for the components of a mixture. The imperfection pressure correction correlation of Figures 21 and 22 should be extended to higher pressures before extensive

use is made of these correlations.

4. The equation proposed for correlating vapor activity coefficients does not completely define γ^V. A method has not been found for correctly determining V values. This indicates that we either do not know enough about V or we do not have the correct function for it. The need for modifications to this equation is indicated.

Recommendations

1. A generalized virial equation of state is required to extend the ideal K-value correlation to higher pressures. This equation of state should be of the density rather than the pressure form. This equation should be applied to the calculation of the imperfection pressure correction by an integration over density rather than pressure.
2. The Scatchard-Hildebrand equation for the liquid activity coefficient is a good first approximation for evaluating this quantity. Modifications of the Scatchard-Hildebrand equation may be needed as the K-value correlation work progresses and ways are found for improving this equation.
3. A new vapor solution theory analogous to the Scatchard-Hildebrand 'regular' solution theory for liquids is needed. This relationship should take into account the composition and character of both solute and solvent as well as temperature effects.

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APPENDIX A

NOMENCLATURE

A - parameter in the Redlich-Kwong equation of state

- parameter in the liquid activity coefficient equation (Equation VI-13)

- parameter in the Beattie-Bridgeman equation of state

- parameter in vapor pressure equation

A_o - parameter in the Benedict-Webb-Rubin equation of state

- parameter in the Beattie-Bridgeman equation of state

a - parameter in the Redlich-Kwong equation of state

- parameter in the Benedict-Webb-Rubin equation of state

- parameter in the Beattie-Bridgeman equation of state

B - second virial coefficient, volume/mole

- parameter in the Redlich-Kwong equation of state

- parameter in the liquid activity coefficient equation (Equation VI-14)

- parameter in vapor pressure equation

B_o - parameter in the Benedict-Webb-Rubin equation of state

- parameter in the Beattie-Bridgeman equation of state

b - generalized second virial coefficient

- parameter in the Beattie-Bridgeman equation of state

- parameter in the Benedict-Webb- Rubin equation of state

- parameter in the Redlich-Kwong equation of state

C - third virial coefficient

C - parameter in vapor pressure equation

c - generalized third virial coefficient

- parameter in the Beattie-Bridgeman equation of state

D - fourth virial coefficient

- parameter in the vapor pressure equation

d - generalized fourth virial coefficient

F - Fahrenheit

f - fugacity, force/area

G - H - TS, Gibbs free energy, energy

K - vapor-liquid equilibrium phase distribution ratio, y/x

M - molecular weight

N_c - number of carbon atoms

P - system pressure, force/area

p° - vapor pressure, force/area

R - universal gas constant

T - temperature

V - volume

v - parameter in liquid volume equation

W - Watson expansion factor, volume/g. mole

x - liquid mole fraction

y - vapor mole fraction

Z - compressibility factor, PV/RT

Greek Symbols

α - parameter in Benedict-Webb-Rubin equation of state

β - reduced second virial coefficient (Equation V-16a)

γ - activity coefficient, $\bar{f}/xf$

- parameter in Benedict-Webb-Rubin equation of state

Δ - change in a property

δ - $(\Delta U/V)^{0.5}$, solubility parameter, (energy/mole-volume)$^{0.5}$

ϵ - parameter in Beattie-Bridgeman equation of state

ω - acentric factor

π - system pressure

- reduced pressure in Beattie-Bridgeman equation of state

ψ - semi-empirical third virial coefficient (Equation V-23)

ν - f/P, pure component fugacity coefficient

ρ - density

ϕ - $\bar{f}/Py$, fugacity coefficient

- ideal reduced volume in Beattie-Bridgeman equation of state

θ - imperfection pressure correction

- reduced temperature in Beattie-Bridgeman equation of state

Σ - summation over all N components in a mixture

Subscripts

1 - component 1 in a mixture (lighter component)

2 - component 2 in a mixture (heavier component)

c - critical property

H - heavy component

HV - heavy component in the vapor phase

i, j - component i or j, respectively

k - convergence property

L - light component

LV - light component in the vapor phase

m - mixture property

r - reduced property

- property at infinite dilution

T - property evaluated at system temperature

Superscripts

° - reference state

- simple fluid property, $\omega = 0$

—— - superbar, partial molar quantity

- volume average property for mixture

E - excess quantity

L - liquid phase

V - vapor phase

' - correction to simple fluid property

- Berlin form of virial equation

Abbreviations

BWR - Benedict-Webb-Rubin

BB - Beattie-Bridgeman

exp - exponential, i.e., e to the power

log - logarithm to the base 10

ln - logarithm to the base e

R-K - Redlich-Kwong

APPENDIX B

EQUATIONS FOR PREDICTION OF VIRIAL COEFFICIENTS

Generalized equations for the second and third virial coefficients are required for the computation of the imperfection pressure correction. It is more important that the equations be of generalized form than they be of highest precision. Virial coefficients for pure components only are required so there is no interest in the interaction coefficients for mixtures.

The expressions presented below are from equations of state and an improved generalized PVT correlation.

Generalized Beattie-Bridgeman Equation of State

The original form of the Beattie-Bridgeman (3) equation is

$$P = \frac{RT}{V^2}(1-\epsilon)(V+B) - \frac{A}{V^2} \qquad \text{(B-1)}$$

where:

$$A = A_o\left(1 - \frac{a}{V}\right)$$

$$B = B_o\left(1 - \frac{b}{V}\right)$$

$$\epsilon = \frac{c}{VT^3}$$

A_o, B_o, a, b, and c are empirical constants

Su and Chang (86) generalized the Beattie-Bridgeman equation as follows:

$$\Pi = \frac{\Theta\,(1-\epsilon')}{\phi^2}(\phi - B') - \frac{A'}{\phi^2} \qquad \text{(B-2)}$$

where:

$$A' = A'_o\left(1 - \frac{a'}{\phi}\right)$$

$$B' = B'_o\left(1 - \frac{b'}{\phi}\right)$$

$$\epsilon' = \frac{c'}{\phi\Theta^3}$$

$\Pi = P/P_c$ = reduced pressure

$\Theta = T/T_c$ = reduced temperature

$\phi = VP_c/RT_c$ = ideal reduced volume

The five generalized constants in the Su-Chang form of the Beattie-Bridgeman equation were given as:

$A'_o = 0.4758$

$a' = 0.1127$

$B'_o = 0.1876$

$b' = 0.0383$

$c' = 0.0500$

This generalized equation is put in the following virial form for the present purposes

$$\frac{PV}{RT} = Z = 1 + \frac{RT_c}{P_c}\left(0.1876 - \frac{0.4758}{\Theta} - \frac{0.050}{\Theta^3}\right)\frac{1}{V}$$

$$+ \left(\frac{RT_c}{P_c}\right)^2\left(\frac{0.046432}{\Theta} - \frac{0.00938}{\Theta^3}\right)\frac{1}{V^2}$$

$$+ \left(\frac{RT_c}{P_c}\right)^3 \left(\frac{0.001058}{\Theta^3}\right) \frac{1}{V^3} \qquad \text{(B-3)}$$

By comparison with the virial equation

$$\frac{PV}{RT} = Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \qquad \text{(B-4)}$$

$$\frac{BP_c}{RT_c} = \left[0.1876 - \frac{0.4758}{T_r} - \frac{0.050}{T_r^3}\right] \qquad \text{(B-5)}$$

$$\frac{C\,P_c^2}{R^2T_c^2} = \left[\frac{0.04643}{T_r} - \frac{0.00938}{T_r^3}\right] \qquad \text{(B-6)}$$

$$\frac{D\,P_c^2}{R^3T_c^3} = \left[\frac{0.001058}{T_r^3}\right] \qquad \text{(B-7)}$$

Benedict-Webb-Rubin Equation of State (7)

For the vapor phase the following short form of the Benedict-Webb-Rubin equation was suggested

$$P = \frac{RT}{V} + \left[B_oRT - A_o - \frac{C_o}{T^2}\right]\frac{1}{V^2} + \left[bRT - a + \frac{c}{T^2}\right]\frac{1}{V^3} \qquad \text{(B-8)}$$

Equation B-8 may be rewritten

$$\frac{PV}{RT} = Z = 1 + \left[B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right]\frac{1}{V} + \left[b - \frac{a}{RT} + \frac{c}{RT^3}\right]\frac{1}{V^2} \qquad \text{(B-9)}$$

The terms in brackets are the second and third virial coefficients.

Canjar et al. (13) give the following general equations for the six constants of Equation B-9

$$A_o = 0.0487\ T_c - 13.01$$

$$B_o = (4.337 \times 10^{-4})\ T_c - 0.0951$$

$$\log_{10} C_o = 0.005497\ T_c + 3.728$$

$$\log_{10} \left(\frac{a}{N_c}\right) = 0.004141\ T_c - 1.941$$

$$\log_{10} (b) = 0.005187\ T_c - 3.498$$

$$\log_{10} C = 0.007521\ T_c + 2.373$$

N_c = number of carbon atoms

$$R = 0.0820544$$

By combining the above six expressions with the bracketed terms in Equation B-9, generalized equations for both the second and third virial coefficients are obtained.

Redlich-Kwong (68) Equation of State

The two constant Redlich-Kwong equation of state has the advantage of being in generalized form

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2} V(V + b)} \qquad \text{(B-10)}$$

where:

$$a = \frac{0.4278\ R^2\ T_c^{2.5}}{P_c}$$

$$b = \frac{0.0867\ RT_c}{P_c}$$

In virial form the Redlich-Kwong equation is

$$\frac{PV}{RT} = Z = 1 + \left(b - \frac{a/RT}{T^{1/2}}\right)\frac{1}{V} + \left(b^2 + \frac{ab/RT}{T^{1/2}}\right)\frac{1}{V^2} + \left(b^3 - \frac{ab^2/RT}{T^{1/2}}\right)\frac{1}{V^3} + \left(b^4 + \frac{ab^3/RT}{T^{1/2}}\right)\frac{1}{V^4} + \ldots \qquad \text{(B-11)}$$

The second, third, fourth and fifth virial coefficients are the terms in brackets. Substitution of the above expression for a and b leads to the following expressions for the second and third virial coefficients

$$B = \left(b - \frac{a/RT}{T^{1/2}}\right) = \frac{0.0867\ RT_c}{P_c}\left[1 - \frac{4.93}{T_r^{1.5}}\right] \qquad \text{(B-12)}$$

$$C = \left(b^2 + \frac{ab}{RT^{3/2}}\right) = \left[\frac{0.0075169\ R^2T_c^2}{P_c^2} + \frac{0.037093\ R^2T_c^2}{T_r^{1.5}P_c^2}\right] \qquad \text{(B-13)}$$

Equations B-12 and B-13 give the second and third virial coefficients in terms of critical constants only. These are the most convenient and simple equations for B and C and should be

considered for this application.

Second Virial Coefficient from Pitzer, et al., Correlation

Pitzer, et al., (62) introduced a characterizing third parameter, ω, called the acentric factor. The acentric factor measures the deviation of the intermolecular potential function of a substance from that of simple spherical molecules. The acentric factor is defined by the reduced vapor pressure at $T_r=0.7$ as follows:

$$\omega = -(\log p_r^o + 1.00)_{T_r=0.7} \qquad \text{(B-14)}$$

The value of the acentric factor is a measure of the deviation from simple PVT behavior. For the simple fluid $\omega=0$. The acentric factor may be approximated from critical properties and the normal boiling point by (20)

$$\omega = \frac{3}{7}\left[\frac{\log P_c, \text{ atm.}}{\frac{T_c}{T_b} - 1.0}\right] - 1.0 \qquad \text{(B-15)}$$

Values of the acentric factor for various substances are presented in Table XXVII.

An improved compressibility factor correlation, using the acentric factor, was recently developed by Pitzer, et al., (51)

$$Z = Z^o + \omega Z' \qquad \text{(B-16)}$$

where: ω = the acentric factor

Z^o = the compressibility factor for the simple fluid

Z' = the correction to the compressibility factor for departure from the simple fluid

Values of Z^o and Z' were originally presented in tabular form (51). They have subsequently been presented in chart form by Edmister (20).

A generalized equation giving a reduced second virial coefficient as a function of reduced temperature and acentric factor was also presented by Pitzer, et al. (62). This equation is

$$\frac{BP_c}{RT_c} = (0.1445 + 0.073\omega) - (0.330 - 0.46\omega)T_r^{-1} - (0.1385 + 0.50\omega)T_r^{-2} - (0.0121 + 0.097\omega)T_r^{-3} - (0.0073\omega)T_r^{-8} \qquad \text{(B-17)}$$

This relationship is shown graphically in Figure 31 and is tabulated as a function of reduced temperature and acentric factor in Table XVII.

Generalized Third Virial Coefficient

An equation for the third virial coefficient, similar to Equation B-17, was not developed by Pitzer, et al. It was thought that such a relationship, if obtainable, would be most convenient for this work.

Values for the third virial coefficient in the Leiden virial equation can be found from compressibility factor data and the second virial coefficient. Using the Pitzer-Curl equation, Equa- B-17, for the second virial coefficient and the Pitzer (51) generalized compilations of Z^o and Z', a generalized equation for the third virial coefficient was derived. The assumption was made

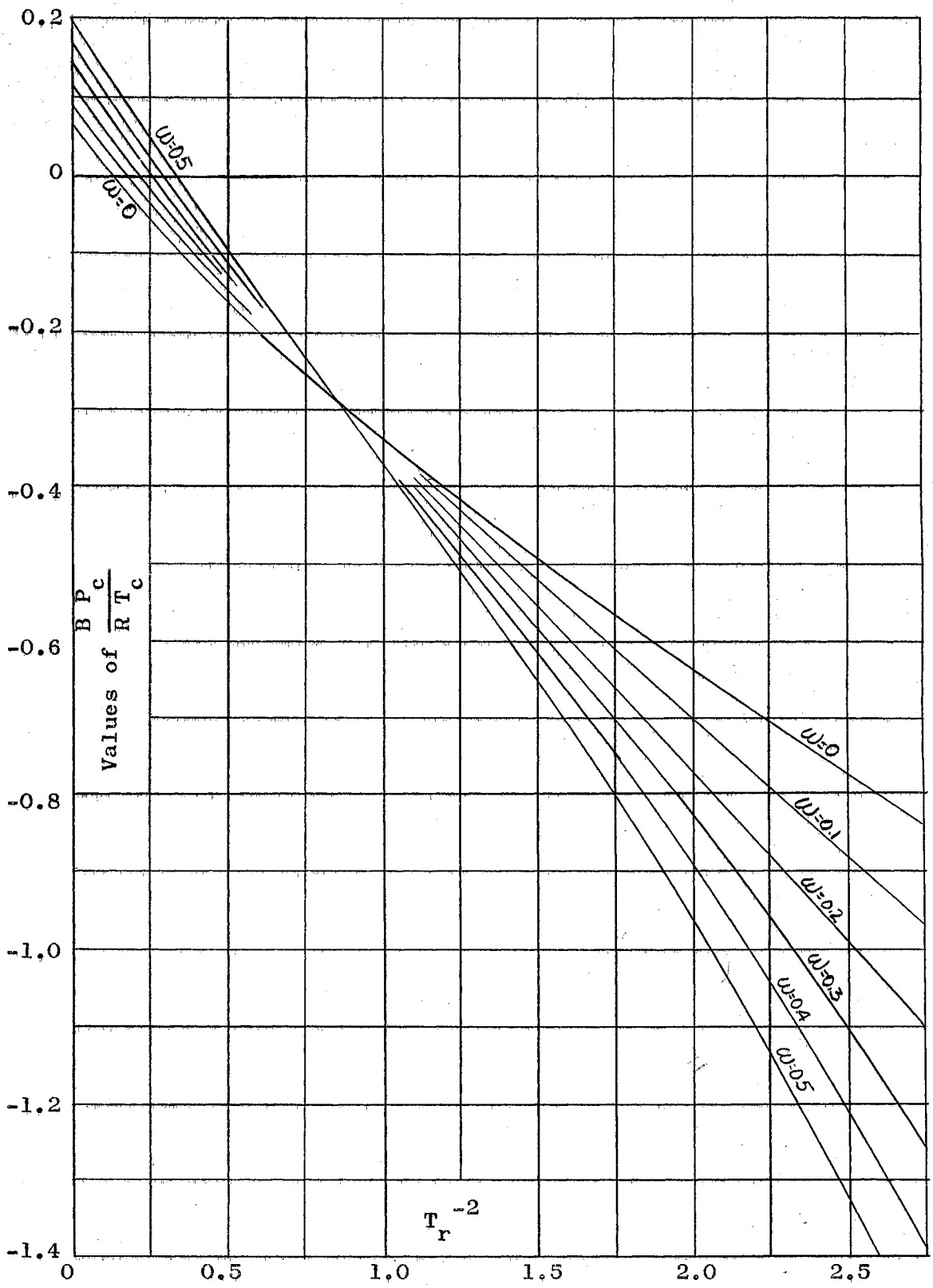

Figure 31

Generalized Second Virial Coefficient(23)

TABLE XVII

GENERALIZED SECOND VIRIAL COEFFICIENT

REDUCED TEMP.	SECOND VIRIAL AT ACENTRIC FACTOR = 0.0	0.1	0.2	0.3	0.4	0.5
.60	-.84624	-.98953	-1.13282	-1.27611	-1.41940	-1.56270
.65	-.73506	-.83356	-.93207	-1.03057	-1.12908	-1.22758
.70	-.64485	-.71482	-.78479	-.85476	-.92473	-.99470
.75	-.57040	-.62094	-.67148	-.72202	-.77256	-.82310
.80	-.50803	-.54466	-.58128	-.61790	-.65452	-.69114
.85	-.45513	-.48139	-.50765	-.53391	-.56017	-.58643
.90	-.40975	-.42807	-.44639	-.46470	-.48302	-.50134
.95	-.37044	-.38253	-.39463	-.40672	-.41882	-.43091
1.00	-.33610	-.34323	-.35036	-.35749	-.36462	-.37175
1.05	-.30586	-.30897	-.31209	-.31520	-.31832	-.32143
1.10	-.27905	-.27888	-.27871	-.27855	-.27838	-.27821
1.15	-.25513	-.25226	-.24938	-.24650	-.24363	-.24075
1.20	-.23368	-.22855	-.22342	-.21829	-.21317	-.20804
1.25	-.21433	-.20732	-.20031	-.19330	-.18629	-.17927
1.30	-.19680	-.18821	-.17961	-.17102	-.16242	-.15383
1.35	-.18085	-.17092	-.16099	-.15106	-.14113	-.13120
1.40	-.16628	-.15522	-.14416	-.13309	-.12203	-.11097
1.45	-.15292	-.14090	-.12888	-.11685	-.10483	-.09281
1.50	-.14064	-.12779	-.11495	-.10211	-.08927	-.07643
1.55	-.12930	-.11576	-.10222	-.08868	-.07514	-.06160
1.60	-.11880	-.10467	-.09053	-.07640	-.06227	-.04813
1.65	-.10906	-.09442	-.07978	-.06514	-.05050	-.03586
1.70	-.10000	-.08493	-.06985	-.05478	-.03971	-.02463
1.75	-.09155	-.07611	-.06067	-.04523	-.02978	-.01434
1.80	-.08365	-.06790	-.05214	-.03639	-.02064	-.00488
1.85	-.07625	-.06023	-.04422	-.02820	-.01218	.00383
1.90	-.06931	-.05307	-.03683	-.02058	-.00434	.01189
1.95	-.06278	-.04635	-.02992	-.01349	.00292	.01935
2.00	-.05663	-.04005	-.02346	-.00688	.00970	.02628

in the development of this equation that the virial equation of state can be terminated after the third virial coefficient term. The equation is presented below

$$\frac{CP_c^2}{R^2T_c^2} = (0.10844 + 0.3895\omega) + (-0.3387 + 1.211\omega)T_r^{-1}$$

$$+ (0.4058 - 1.304\omega)T_r^{-2} + (-0.1358 + 0.478\omega)T_r^{-3} \qquad \text{(B-18)}$$

This relationship is shown graphically in Figure 32 and is tabulated as a function of reduced temperature and acentric factor in Tables XVIII and XIX. The procedure used in the development of Equation B-18 is presented in Appendix E.

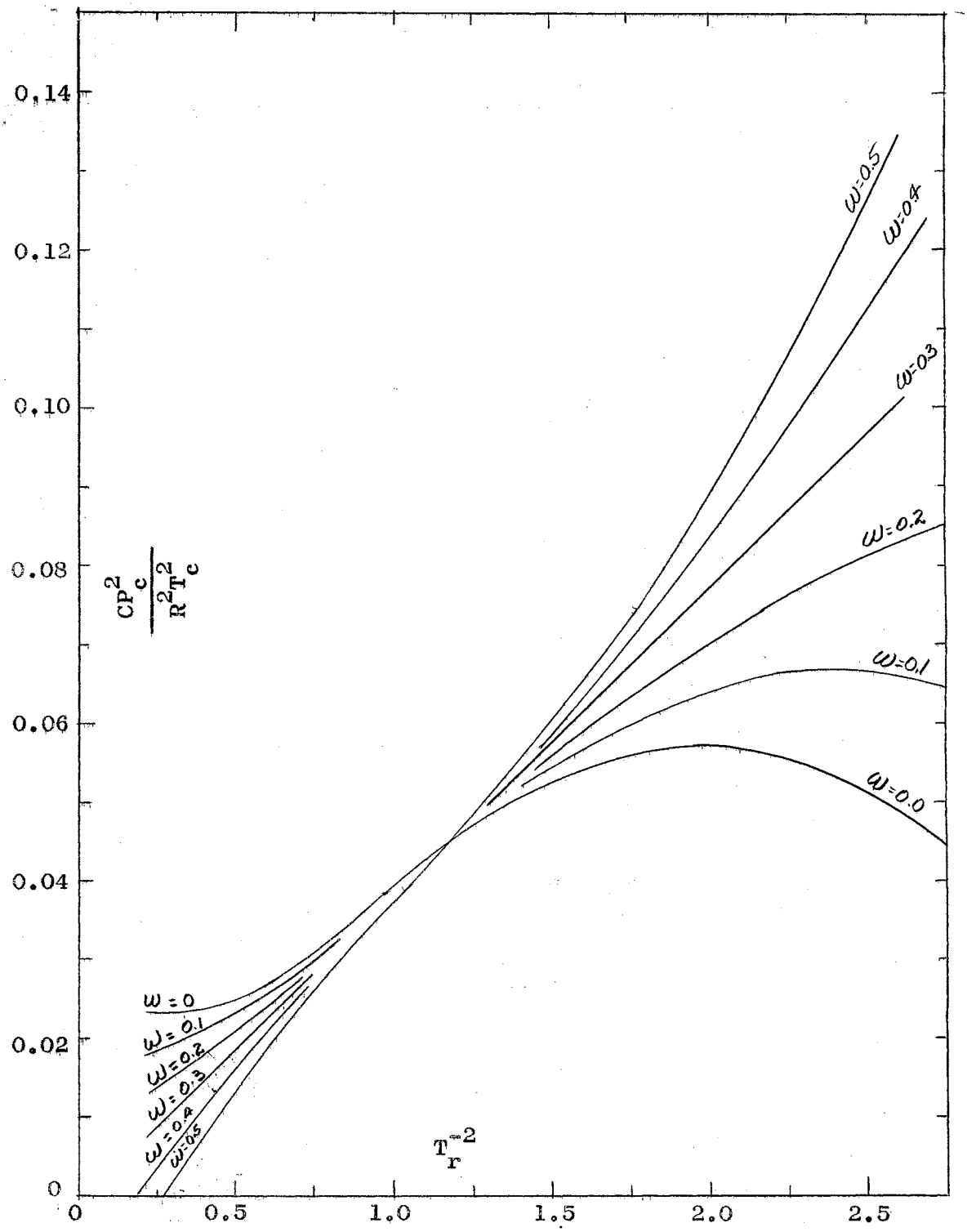

Figure 32

Generalized Third Virial Coefficient

Approximation

TABLE XVIII

GENERALIZED THIRD VIRIAL COEFFICIENT

REDUCED TEMP.	THIRD VIRIAL AT ACENTRIC FACTOR = 0.0	0.1	0.2	0.3	0.4	0.5
.60	.04245	.06422	.08598	.10774	.12951	.15127
.65	.05334	.06595	.07856	.09116	.10377	.11638
.70	.05682	.06397	.07111	.07825	.08540	.09254
.75	.05636	.06023	.06411	.06798	.07186	.07573
.80	.05389	.05581	.05774	.05966	.06159	.06351
.85	.05050	.05127	.05204	.05282	.05359	.05437
.90	.04681	.04691	.04701	.04711	.04721	.04731
.95	.04316	.04287	.04258	.04229	.04200	.04171
1.00	.03974	.03922	.03870	.03818	.03766	.03714
1.05	.03663	.03596	.03530	.03463	.03397	.03330
1.10	.03387	.03310	.03232	.03155	.03078	.03001
1.15	.03147	.03060	.02972	.02885	.02798	.02711
1.20	.02940	.02843	.02745	.02648	.02550	.02453
1.25	.02766	.02656	.02546	.02437	.02327	.02217
1.30	.02620	.02496	.02372	.02248	.02124	.02000
1.35	.02501	.02361	.02220	.02079	.01939	.01798
1.40	.02406	.02246	.02086	.01927	.01767	.01607
1.45	.02331	.02150	.01970	.01789	.01608	.01427
1.50	.02275	.02071	.01867	.01663	.01459	.01255
1.55	.02236	.02007	.01778	.01549	.01320	.01090
1.60	.02211	.01955	.01699	.01444	.01188	.00932
1.65	.02199	.01915	.01631	.01347	.01063	.00780
1.70	.02197	.01884	.01571	.01258	.00945	.00632
1.75	.02206	.01863	.01519	.01176	.00833	.00489
1.80	.02223	.01849	.01474	.01100	.00725	.00351
1.85	.02247	.01841	.01435	.01029	.00622	.00216
1.90	.02278	.01840	.01401	.00963	.00524	.00086
1.95	.02315	.01843	.01372	.00901	.00430	-.00041
2.00	.02356	.01852	.01348	.00843	.00339	-.00164

TABLE XIX

COEFFICIENTS FOR GENERALIZED

THIRD VIRIAL COEFFICIENT

EQUATION

REDUCED TEMP.	THIRD VIRIAL FOR SIMPLE FLUID	CHANGE OF C WITH ACENTRIC FACTOR
.60	.04245	.21762
.65	.05334	.12608
.70	.05682	.07143
.75	.05636	.03873
.80	.05389	.01925
.85	.05050	.00773
.90	.04681	.00100
.95	.04316	-.00289
1.00	.03974	-.00520
1.05	.03663	-.00665
1.10	.03387	-.00772
1.15	.03147	-.00870
1.20	.02940	-.00975
1.25	.02766	-.01097
1.30	.02620	-.01240
1.35	.02501	-.01406
1.40	.02406	-.01596
1.45	.02331	-.01808
1.50	.02275	-.02040
1.55	.02236	-.02290
1.60	.02211	-.02557
1.65	.02199	-.02838
1.70	.02197	-.03130
1.75	.02206	-.03433
1.80	.02223	-.03744
1.85	.02247	-.04062
1.90	.02278	-.04385
1.95	.02315	-.04712
2.00	.02356	-.05042

APPENDIX C

MOLAR LIQUID VOLUMES

The value chosen for the molar liquid volume in Equation V-16 is very important. In some of the previous applications a saturated liquid volume was used. While theoretically sound, this is not practical for this work because values of the imperfection pressure correction are required at temperatures above the critical point, which would be the upper limit for the saturated liquid volume.

Molar liquid volumes are also required in the application of the Scatchard-Hildebrand (83,89,90) equation for the liquid activity coefficient. For this purpose, V_i^L has been computed by the Watson (28) equation. Chao and Seader (15) used a fixed value independent of temperature. It is of interest to review and compare a few of the methods for calculating molar liquid volumes.

There are two generalized compressibility factor correlations worthy of note for saturated liquids. Meissner et al. (55) made such a correlation several years ago. This correlation was used by Scheibel (79) in his evaluation of the imperfection pressure correction. Pitzer et al. (62) recently presented an improved compressibility factor correlation, one part of which was for saturated liquids. Values of the volume at the saturated liquid state are not of much value for this work.

Gamson and Watson (28) introduced the following empirical equation for calculating the hypothetical molar liquid volume

$$V_i^L = V_1 W_1 \ (5.7 + 3.0 \ T_r) \qquad \text{(C-1)}$$

where V_i^L = molar liquid volume, cc/ g. mole

$V_1 W_1$ = reference volume-expansion factor product in the same units as V_i^L

T_r = reduced temperature

Equation C-1 is a special case of a more complete correlation that includes a pressure effect (88). The quantity $V_1 W_1$ is the product of a molar liquid volume of the component at some measurable state and the expansion factor at the same state. This product is a constant for each substance and is established by a single density measurement and the corresponding value of W. The volume calculated via Equation C-1 represents the volume of a hypothetical incompressible liquid, since no provisions are made for the influence of pressure.

Background for Equation C-1

In the development of a generalization for liquid properties, Watson (88) started by applying to the liquid phase the gas phase relation

$$PV = ZRT \qquad \text{(C-2)}$$

The compressibility factor, Z, is a function of reduced temperature and pressure, and is approximately the same for all substances at the same reduced temperature and pressure.

If Equation C-2 is applied to the liquid phase, an expression for the liquid density may be obtained.

$$\rho = \frac{PM}{ZRT} = \frac{P_r}{ZRT_r}\frac{P_c M}{T_c} = \frac{WP_c M}{T_c} \qquad (C\text{-}3)$$

The above equation suggests that W, the expansion factor, is a function of reduced temperature and pressure only, i.e.,

$$W = \frac{P_r}{ZRT_r} \quad (\text{units of } R^{-1}) \qquad (C\text{-}4)$$

See note on page 153 for clarification of units of W.

Watson found that W is not a generalized function of reduced conditions. He found that W varied as much as 20 per cent for different compounds at the same reduced conditions.

Watson demonstrated that more exact results can be obtained by applying the expression

$$V = V_1 W_1 / W \qquad (C\text{-}5)$$

in conjunction with a W correlation in terms of T_r and P_r for one material. This equation is claimed to give reasonable accuracy, that is, a maximum deviation of five per cent from true values at pressures up to and including the critical point.

Iso- and n-pentane were used by Watson to prepare the first expansion factor plot (88). Recently, Ritter, Lenoir and Schweppe (70) have published a purportedly improved correlation for the expansion factor.

Equation C-5 is used to determine the unknown molar volume of any substance at a specific temperature and pressure when

some measured value of V_l is available at a known temperature and pressure. Both values of W are read from the expansion factor plot at the corresponding reduced temperatures and pressures.

By comparing Equations C-1 and C-5, it is seen that the simplified empirical expression for W is

$$1/W = (5.7 + 3.0\ T_r) \qquad (C\text{-}6)$$

W was selected at sufficiently high pressures such that pressure has no effect on the liquid phase. The term $(5.7 + 3.0\ T_r)$ corresponds to 1/W for the hypothetical incompressible liquid reference state. This value is a linear extrapolation of 1/W from the absolute zero and thus defines the liquid standard state as having a constant volumetric coefficient of expansion equal to that of the real liquid at the absolute zero. The constant (5.7) is in effect a common multiplier for $V_l W_l$ which yields the extrapolated molar liquid volume at absolute zero temperature. The constant (3.0) established the fixed volumetric coefficient of expansion which holds at absolute zero temperature and at all other temperatures.

At low reduced temperatures the liquid volumes calculated from Equation C-1 differ little from actual molar liquid volumes. As the critical is approached, the calculated volume is smaller than the actual molar volume except at high pressures.

Modification of the Watson Volume Expression

For rapid calculation of molar volumes, a tabulation of values of $V_l W_l$ for various substances is most useful. Values of

V_1W_1 have not been centrally tabulated in the literature, neither have they been evaluated for all substances of interest. Having worked under the above limitations, it was felt that there was sufficient justification for developing a method for predicting molar liquid volumes which would be applicable to all substances and be convenient for digital computer calculations. The procedure used in developing this new correlation is outlined below:

1. A tabulation was prepared of various substances with their respective Watson expansion factor and acentric factor.

2. The ideal critical volume for each substance is defined and calculated by

$$V_{c_i} = \frac{RT_{c_i}}{P_{c_i}} \qquad \text{(C-7)}$$

3. A 'reduced expansion factor' was then calculated.

$$v' = \frac{V_1W_1}{V_{c_i}} = \frac{P_{c_i}V_1W_1}{RT_{c_i}} \qquad \text{(C-8)}$$

4. The 'reduced expansion factor' was plotted as a function of acentric factor (Figure 33).

5. The following equation was fitted to the plot of reduced expansion factor vs. acentric factor (Curve A, Figure 33).

$$v' = 0.01361 - 0.00328\omega - 0.0244\omega^2 + 0.0599\omega^3 - 0.0308\omega^4 \qquad \text{(C-9)}$$

Curve B was found to be a more useful relationship for this work. The fitted equation for this curve is

$$v' = 0.01361 - 0.00436\omega \qquad \text{(C-10)}$$

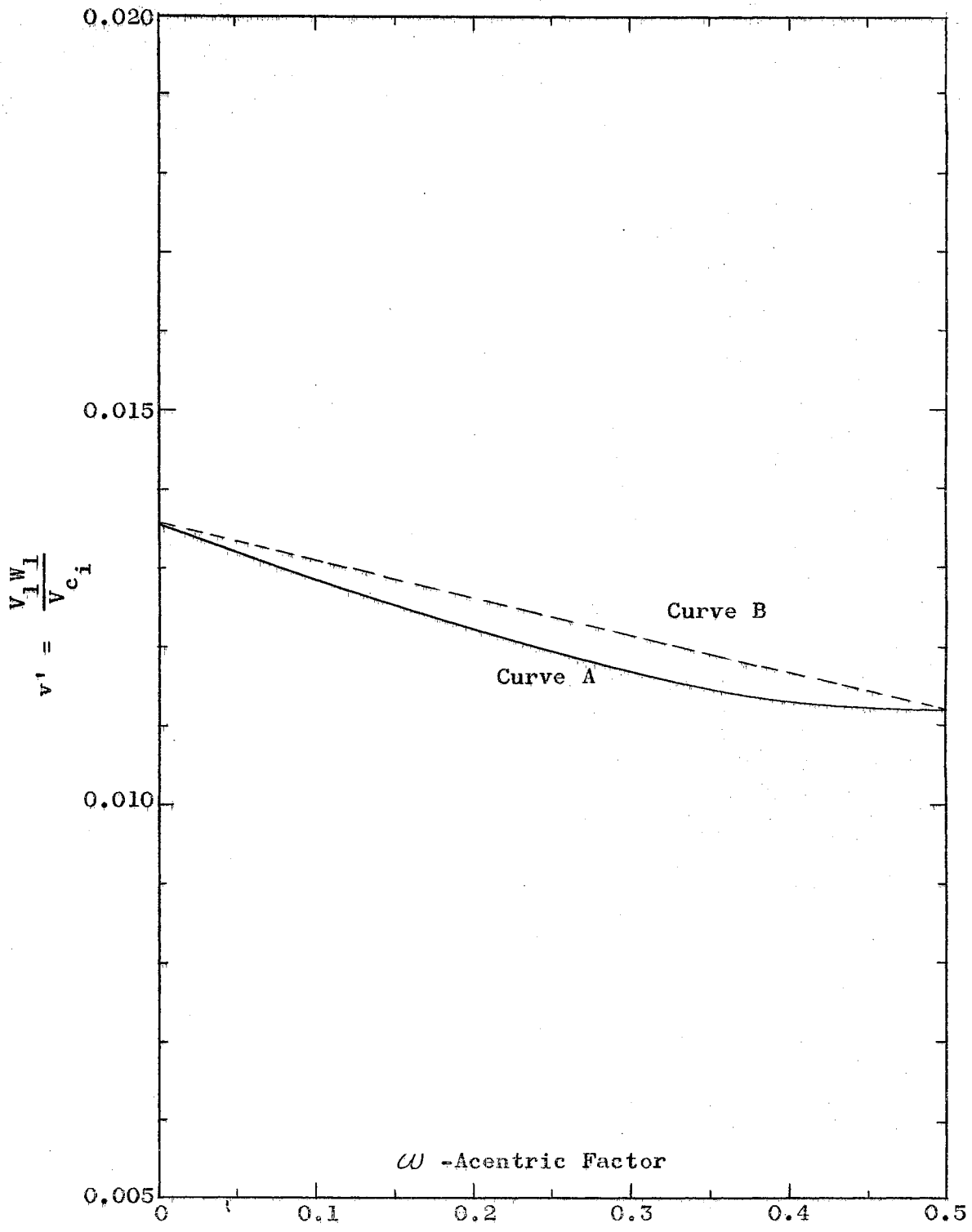

Figure 33

v' as a Function of Acentric Factor

6. The reduced volume may then be calculated using an equation of the form of the Watson equation

$$V_{r_i} = v'(5.7 + 3.0\ T_r) \qquad \text{(C-11)}$$

Values of V_{r_i} as a function of T_r and ω are tabulated in Table XX and presented graphically in Figure 34.

7. The molar liquid volume is then calculated by

$$V_i^L = \frac{RT_{c_i} V_{r_i}}{P_{c_i}} \qquad \text{(C-12)}$$

8. Equation C-11 can be rewritten such that the reduced volume is a function of reduced temperature and acentric factor.

$$V_{r_i} = V_{r_i}^o + \omega(V'_{r_i}) \qquad \text{(C-13)}$$

Values of $V_{r_i}^o$ and V'_{r_i} are tabulated in Table XXI.

Molar liquid volumes were evaluated for liquid propane using the methods of Chao-Seader (15), Meissner and Redding (55), Watson (28) and Equations C-10 through C-12. The results of these calculations are plotted as a function of reduced temperature in Figure 35.

It is obvious from this plot that the constant volume value of Chao and Seader is an oversimplification and that the saturated liquid curve of Meissner and Redding cannot be extrapolated to higher temperatures with any success. There is excellent agreement of the volumes calculated via Equations C-1 and the volumes calculated via Equations C-10 through C-12.

Edmister (20) compared observed saturated liquid volumes

TABLE XX

REDUCED LIQUID VOLUME VIA EQUATION C-6

REDUCED TEMP.	REDUCED VOLUME AT ACENTRIC FACTOR = 0.0	0.1	0.2	0.3	0.4	0.5
.60	.10207	.09880	.09552	.09225	.08898	.08570
.65	.10411	.10077	.09743	.09409	.09075	.08742
.70	.10615	.10275	.09934	.09594	.09253	.08913
.75	.10819	.10472	.10125	.09778	.09431	.09084
.80	.11024	.10670	.10316	.09963	.09609	.09256
.85	.11228	.10868	.10508	.10147	.09787	.09427
.90	.11432	.11065	.10699	.10332	.09965	.09599
.95	.11636	.11263	.10890	.10516	.10143	.09770
1.00	.11840	.11460	.11081	.10701	.10321	.09941
1.05	.12044	.11658	.11272	.10885	.10499	.10113
1.10	.12249	.11856	.11463	.11070	.10677	.10284
1.15	.12453	.12053	.11654	.11254	.10855	.10456
1.20	.12657	.12251	.11845	.11439	.11033	.10627
1.25	.12861	.12448	.12036	.11623	.11211	.10798
1.30	.13065	.12646	.12227	.11808	.11389	.10970
1.35	.13269	.12844	.12418	.11992	.11567	.11141
1.40	.13473	.13041	.12609	.12177	.11745	.11313
1.45	.13678	.13239	.12800	.12362	.11923	.11484
1.50	.13882	.13436	.12991	.12546	.12101	.11656
1.55	.14086	.13634	.13182	.12731	.12279	.11827
1.60	.14290	.13832	.13373	.12915	.12457	.11998
1.65	.14494	.14029	.13564	.13100	.12635	.12170
1.70	.14698	.14227	.13755	.13284	.12813	.12341
1.75	.14902	.14424	.13947	.13469	.12991	.12513
1.80	.15107	.14622	.14138	.13653	.13169	.12684
1.85	.15311	.14820	.14329	.13838	.13347	.12855
1.90	.15515	.15017	.14520	.14022	.13524	.13027
1.95	.15719	.15215	.14711	.14207	.13702	.13198
2.00	.15923	.15412	.14902	.14391	.13880	.13370

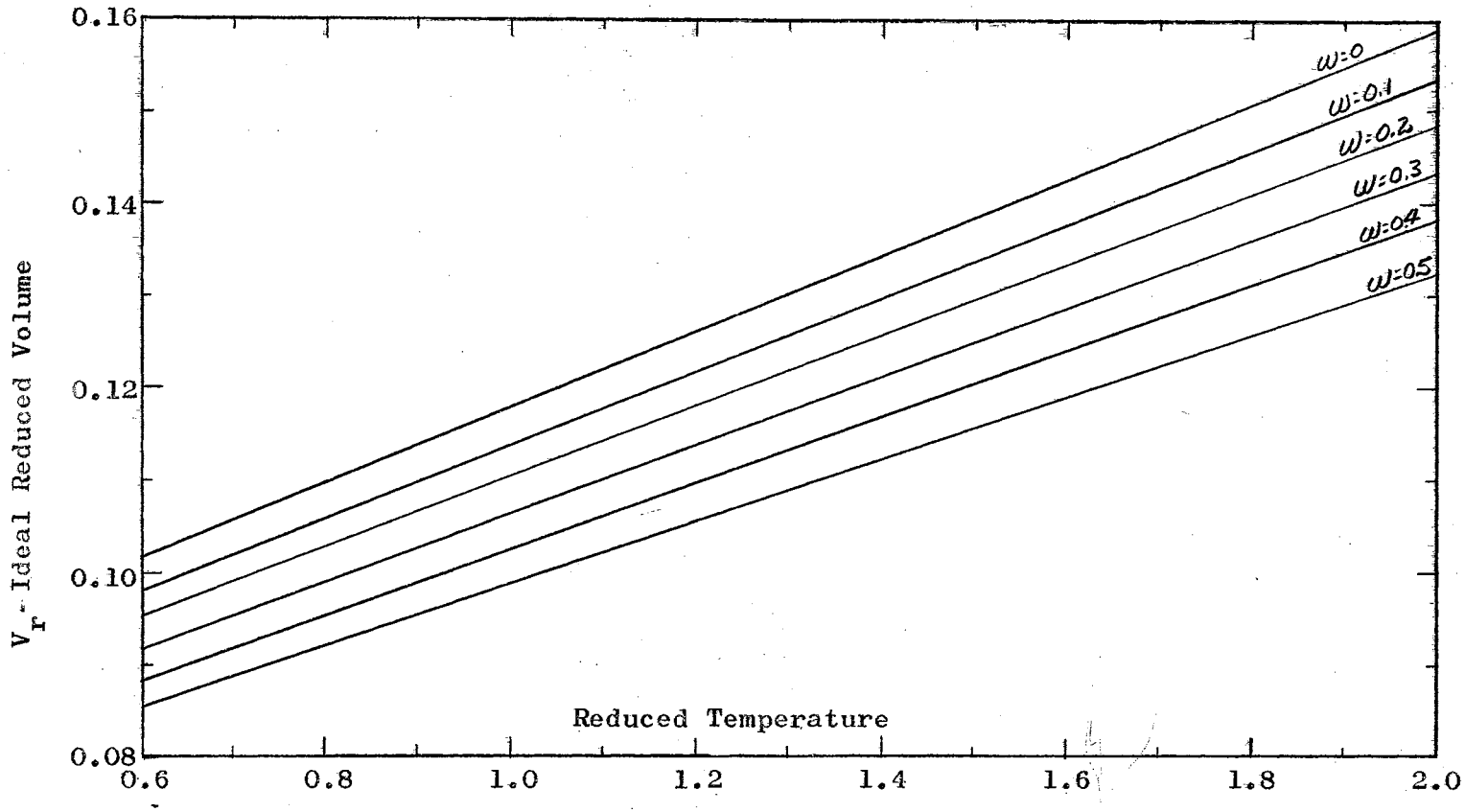

Figure 34

Reduced Volume for Real and Hypothetical Liquids

TABLE XXI

REDUCED VOLUME FOR A SIMPLE FLUID

VOLUME CORRECTION TO SIMPLE FLUID

REDUCED TEMP.	REDUCED VOLUME SIMPLE FLUID	ACENTRIC FACTOR CORRECTION
.60	.10207	-.03273
.65	.10411	-.03339
.70	.10615	-.03404
.75	.10819	-.03470
.80	.11024	-.03535
.85	.11228	-.03601
.90	.11432	-.03666
.95	.11636	-.03732
1.00	.11840	-.03797
1.05	.12044	-.03863
1.10	.12249	-.03928
1.15	.12453	-.03993
1.20	.12657	-.04059
1.25	.12861	-.04124
1.30	.13065	-.04190
1.35	.13269	-.04255
1.40	.13473	-.04321
1.45	.13678	-.04386
1.50	.13882	-.04452
1.55	.14086	-.04517
1.60	.14290	-.04583
1.65	.14494	-.04648
1.70	.14698	-.04714
1.75	.14902	-.04779
1.80	.15107	-.04845
1.85	.15311	-.04910
1.90	.15515	-.04976
1.95	.15719	-.05041
2.00	.15923	-.05107

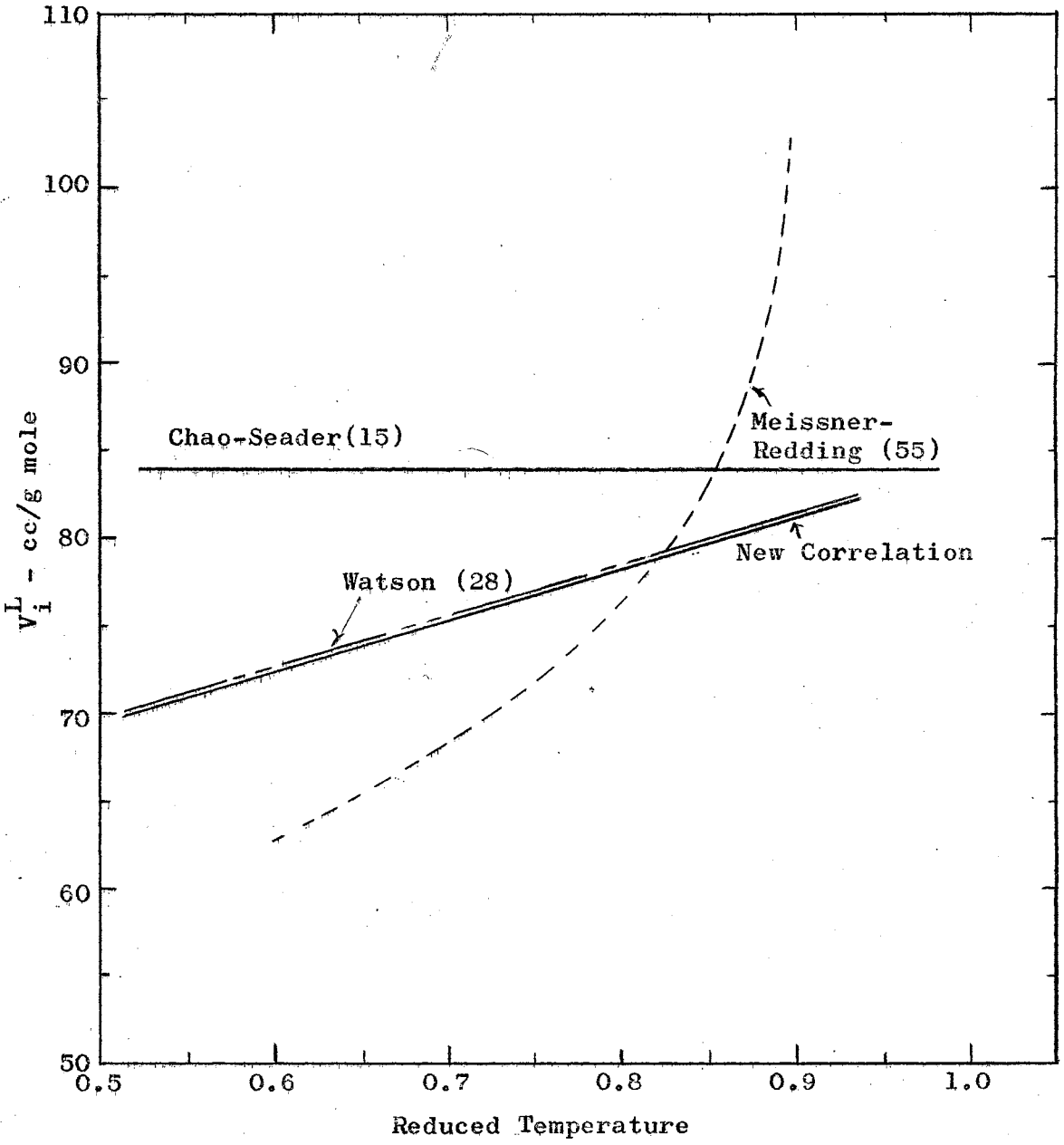

Figure 35

Comparison of Molal Liquid Volumes from

Different Sources for Propane

with those calculated via Equation C-1. The calculated volumes are lower than the observed volumes. One would expect the values calculated via Equations C-10 through C-12 to also be lower than observed volumes. This difference indicates the need for more work to improve methods for calculating molar liquid volumes. This work does not appear to be justified at this time. It is thought that the volumes predicted via Equations C-10 through C-12 are adequate for this work.

A note to clarify the dimension of W in Equation C-4 is in order. As defined by Watson (88) in 1943, the expansion factor, W, had the dimension of R^{-1}. The ordinate of Figure 33 also has dimension of R^{-1} (i.e., 1/82.06). The term W could be a dimensionless factor, if defined as

$$W = P_r/ZT_r = \rho/\rho_{c_i} = V_{c_i}/V \qquad \text{(C-14)}$$

where: $\rho_{c_i} = 1/V_{c_i} = P_c/RT_c$

ρ_{c_i} = ideal critical density

V_{c_i} = ideal critical volume

If W is defined in this way, the ordinate of Figure 33 would be increased by a factor of 82.06. The term v' of Equations C-8 through C-10 and Figure 33 has the units of R^{-1}. The term $(5.7 + 3.0\ T_r)$ in Equations C-1, C-6 and C-11 has the dimensions of R, making V_{r_i} of Equations C-11 and C-13 dimensionless.

APPENDIX D

EVALUATION OF VAPOR PRESSURES

At fairly high reduced temperatures hydrogen and nitrogen show a reverse solubility, i.e., the concentration of the gas in the solvent increases with increasing temperature. In view of this phenomenon, it was thought that at high reduced temperatures K_{Ideal} should go through a maximum and then decrease as temperature is increased at constant pressure.

One of the problems encountered in the development of a K_{Ideal} correlation via the imperfection pressure correction is the choice of the value for vapor pressure in Equations V-14 and V-19. The value of θ, the imperfection pressure correction, at higher reduced temperatures depends on the form of the vapor pressure equation. Specifically, the problem is the choice of the vapor pressure for reduced temperatures greater than unity. It is possible that a vapor pressure equation could be chosen such that the K_{Ideal} correlation failed to show the reverse solubility effect known to exist at the higher temperatures.

Several empirical vapor pressure equations were studied in order to determine the form of these equations when they are extrapolated above unity reduced temperature. Some of the better known equations are tabulated below

$$\log p^{o} = A - B/(C + T) \qquad \text{(D-1a)}$$

$$\log p^{o} = A - B/T + C \log T \qquad \text{(D-1b)}$$

$$\log p^{o} = A - B/T - C \log T + DT \qquad \text{(D-1c)}$$

$$\log p^{o} = A - B/T - C \log T + DT^{n} \quad (n>1) \qquad \text{(D-1d)}$$

$$\log p^{o} = A - B/T - DT + ET^{2} \qquad \text{(D-1e)}$$

$$\log p^{o} = A - B/T - C \log T + Dp^{o}/T^{2} \qquad \text{(D-1f)}$$

$$\log p^{o} = A - B/T - C/T^{2} \qquad \text{(D-1g)}$$

Equations D-1b through D-1e approach infinity as T approaches infinity. Equations D-1a and D-1g approach the constant value A as T approaches infinity. Equation D-1f approaches negative infinity as T approaches infinity.

If the vapor pressure approaches infinity as the reduced temperature approaches infinity, then the requirement that K_{Ideal} go through a maximum when the reduced temperature is increased at constant pressure cannot be satisfied. Therefore, we must eliminate from consideration those vapor pressure equations with the above mentioned property.

Equations D-1a and D-1f were selected for additional study. Equation D-1a, the Antoine equation, is accurate only over a small pressure range. Equation D-1f is accurate over the complete vapor pressure range, but the equation has no roots at values of reduced temperatures much above unity. This was enough evidence to eliminate these two equations.

The generalized equation of Reidel (69) was next studied. As the reduced temperature approaches infinity, the vapor pressure approaches infinity, therefore, this method of vapor pressure evaluation must be discarded.

Pitzer et al. (51) correlated vapor pressures for reduced

temperatures less than unity as follows:

$$\ln p_r^o = (\ln p_r^o)^o + \omega \left(\frac{\partial \ln p_r^o}{\partial \omega} \right)_T \qquad \text{(D-2)}$$

where: $(\ln p_r^o)^o$ is the log of the vapor pressure for a simple fluid

$\left(\frac{\partial \ln p_r^o}{\partial \omega} \right)_T$ represents the change of the vapor pressure with acentric factor

From the difinition of the acentric factor $(\ln p_r^o)^o = -2.303$ and $(\partial \ln p_r^o / \partial \omega) = -2.303$ at $T_r = 0.7$.

Pitzer et al.(51) tabulated values of these two vapor pressure terms as functions of reduced temperature only. A straight line extrapolation of these values has been made in the region of $T_r > 1.0$. Equations have been derived for the components of the generalized vapor pressure equation to permit computer application of Equation D-2. The equation for the log of the vapor pressure of a simple fluid is

$$(\ln p_r^o)^o = 5.366 - (5.366/T_r) \qquad \text{(D-3)}$$

It was necessary to divide the plot of $(\partial \ln p_r^o / \partial \omega)$ into three parts to get an accurate fit of the data. For $T_r < 1.0$

$$\left(\frac{\partial \ln p_r^o}{\partial \omega} \right)_T = 2.415 - (0.7116/T_r) - (1.179/T_r^2) + (0.7072/T_r^3) + (0.1824/T_r^4) \qquad \text{(D-4)}$$

For $T_r > 1.0$

$$\left(\frac{\partial \ln p_r^o}{\partial \omega}\right)_T = 5.179 - (5.133/T_r) - (0.4566/T_r^2) \qquad (D\text{-}5)$$

For $T_r = 1.0$

$$\left(\frac{\partial \ln p_r^o}{\partial \omega}\right)_T = 0.0 \qquad (D\text{-}6)$$

Values of $(\ln p_r^o)^o$ and $(\partial \ln p_r^o/\partial\omega)$ calculated via Equations D-3 through D-6 are tabulated in Table XXII. Reduced vapor pressures, calculated from these same equations and Equation D-2, as a function of reduced temperature and acentric factor, are tabulated in Table XXIII.

Yarborough (93), using the above method for evaluating vapor pressures, evaluated K_{Ideal} for several components. Values of Θ, the imperfection pressure correction, were obtained from the tentative generalized correlation of this quantity available at the time these calculations were made (60). K_{ideal} was then obtained from these Θ values via Equation V-22. A summary of these calculations made is presented in Table XXIV. Plots of K_{Ideal} as a function of reduced temperature at constant reduced pressure are presented for various compounds in Figures 36 through 41.

The calculated value of K_{Ideal} does go through a maximum as the reduced temperature increases for all components except hydrogen (using the acentric factor for hydrogen as -0.237). The K_{Ideal} values for methane and nitrogen go through a maximum only at high reduced pressures.

The acentric factor for hydrogen of -0.237 is the value obtained via Equation B-15. This was the value used for hydrogen

TABLE XXII

COEFFICIENTS FOR GENERALIZED

VAPOR PRESSURE EQUATION

REDUCED TEMP.	LN VAPOR PRESSURE SIMPLE FLUID	LN VAPOR PRESSURE CHANGE WITH ACENTRIC FACTOR
.60	-3.57701	-3.91208
.65	-2.88912	-3.02312
.70	-2.29951	-2.30934
.75	-1.78850	-1.72920
.80	-1.34138	-1.25219
.85	-.94685	-.85573
.90	-.59616	-.52290
.95	-.28239	-.24092
1.00	-.00000	.00000
1.05	.25550	.24868
1.10	.48777	.47457
1.15	.69985	.68067
1.20	.89425	.86947
1.30	1.23819	1.20321
1.35	1.39106	1.35142
1.25	1.07310	1.04306
1.40	1.53300	1.48897
1.45	1.66516	1.61698
1.50	1.78850	1.73641
1.55	1.90389	1.84809
1.60	2.01207	1.95275
1.65	2.11369	2.05103
1.70	2.20933	2.14350
1.75	2.29951	2.23066
1.80	2.38467	2.31296
1.85	2.46524	2.39079
1.90	2.54156	2.46450
1.95	2.61397	2.53441
2.00	2.68276	2.60081

TABLE XXIII

GENERALIZED VAPOR PRESSURES

REDUCED TEMP.	REDUCED VAPOR PRESSURE AT ACENTRIC FACTOR = 0.0	0.1	0.2	0.3	0.4	0.5
.60	.02795	.01890	.01278	.00864	.00584	.00011
.65	.05562	.04111	.03038	.02245	.01659	.01012
.70	.10030	.07962	.06320	.05017	.03982	.03013
.75	.16720	.14065	.11832	.09953	.08372	.07014
.80	.26148	.23070	.20355	.17959	.15845	.13015
.85	.38795	.35614	.32693	.30011	.27550	.25016
.90	.55091	.52285	.49621	.47093	.44694	.42017
.95	.75397	.73602	.71850	.70140	.68470	.66018
1.00	1.00000	1.00000	1.00000	1.00000	1.00000	1.00019
1.05	1.29110	1.32361	1.35694	1.39111	1.42614	1.46020
1.10	1.62868	1.70784	1.79084	1.87788	1.96915	2.06021
1.15	2.01345	2.15527	2.30708	2.46959	2.64354	2.82022
1.20	2.44551	2.66766	2.90998	3.17433	3.46268	3.77023
1.25	2.92444	3.24596	3.60282	3.99892	4.43856	4.92024
1.30	3.44939	3.89042	4.38785	4.94888	5.58164	6.29025
1.35	4.01911	4.60068	5.26639	6.02844	6.90075	7.89026
1.40	4.63208	5.37578	6.23889	7.24057	8.40307	9.75027
1.45	5.28653	6.21435	7.30501	8.58708	10.09417	11.86028
1.50	5.98052	7.11460	8.46374	10.06871	11.97803	14.24029
1.55	6.71199	8.07445	9.71347	11.68520	14.05717	16.91030
1.60	7.47879	9.09156	11.05212	13.43546	16.33276	19.85031
1.65	8.27874	10.16342	12.47714	15.31760	18.80468	23.08032
1.70	9.10964	11.28737	13.98570	17.32908	21.47172	26.60033
1.75	9.96930	12.46067	15.57465	19.46682	24.33166	30.41034
1.80	10.85556	13.68053	17.24066	21.72724	27.38139	34.50035
1.85	11.76632	14.94415	18.98025	24.10642	30.61705	38.88036
1.90	12.69952	16.24872	20.78984	26.60009	34.03416	43.54037
1.95	13.65319	17.59148	22.66578	29.20377	37.62766	48.48038
2.00	14.62544	18.96972	24.60441	31.91281	41.39206	53.68039

TABLE XXIV

SUMMARY OF IDEAL K-VALUE CALCULATIONS

FOR VARIOUS SUBSTANCES

T_R	LN θ°	LN θ'	IMPERFECTION PRESSURE CORRECTION					VAPOR PRESSURE	
			H_2	N_2	CH_4	C_3H_8	I-C_5	H_2	N_2
REDUCED PRESSURE = 0.5									
0.60	-0.70	-1.16	0.654	0.476	0.490	0.416	0.386	0.066	0.024
0.75	-0.28	-0.33	0.817	0.747	0.754	0.719	0.703	0.255	0.157
0.90	0.01	-0.13	0.960	1.005	0.989	0.970	0.963	0.636	0.540
1.20	0.66	0.71	1.636	1.982	1.950	2.155	2.257	1.970	2.510
1.50	1.30	2.00	2.283	3.940	3.740	4.980	5.660	3.900	6.400
2.00	1.90	4.60	2.249	7.870	7.000	14.450	18.100	7.650	16.100
REDUCED PRESSURE = 1.0									
0.60	-1.41	-2.14	3.405	0.226	0.239	0.176	0.153	0.066	0.025
0.75	-0.69	-0.64	0.584	0.490	0.498	0.455	0.436	0.255	0.157
0.90	-0.25	-0.23	0.823	0.773	0.777	0.752	0.741	0.636	0.540
1.20	0.48	0.74	1.357	1.660	1.627	1.809	1.900	1.970	2.510
1.50	1.16	2.03	1.970	3.430	3.260	4.340	4.950	3.900	6.400
2.00	1.80	4.64	2.013	7.120	6.320	12.250	16.600	7.650	13.100
REDUCED PRESSURE = 2.0									
0.60	-2.70	-3.87	3.168	0.059	0.065	0.037	0.029	0.066	0.025
0.75	-1.47	-1.16	0.302	0.220	0.227	0.193	0.178	0.255	0.157
0.90	00.74	-0.37	0.532	0.476	0.476	0.451	0.440	0.636	0.540
1.20	0.15	0.80	0.961	1.195	1.171	1.312	1.382	1.970	2.510
1.50	0.89	2.11	1.477	2.620	2.488	3.360	3.845	3.900	6.400
2.00	1.59	4.70	1.611	5.790	5.140	10.030	13.600	7.650	16.100
REDUCED PRESSURE = 5.0									
0.60	-5.36	-6.66	0.023	0.003	0.005	0.002	0.001	0.066	0.025
0.75	-3.17	-2.04	0.068	0.039	0.041	0.031	0.027	0.255	0.157
0.90	-1.91	-0.62	0.171	0.145	0.147	0.134	0.129	0.636	0.540
1.20	-0.70	0.90	0.402	0.513	0.543	0.570	0.604	1.970	2.510
1.50	0.18	2.22	0.708	1.294	1.224	1.680	1.938	3.900	6.400
2.00	1.07	4.83	0.928	3.450	3.060	6.090	8.310	7.650	16.100

TABLE XXIV (CONTINUED)

SUMMARY OF IDEAL K-VALUE CALCULATIONS

FOR VARIOUS SUBSTANCES

T_R	VAPOR PRESSURE			IDEAL K-VALUES					
	CH_4	C_3H_8	I-C_5	H_2 ω=-.237	H_2 ω=0.0	N_2	CH_4	C_3H_8	I-C_5
REDUCED PRESSURE = 0.5									
0.60	0.027	0.016	0.012	0.202	0.271	0.105	0.110	0.075	0.063
0.75	0.163	0.125	0.111	0.623	0.675	0.420	0.433	0.348	0.316
0.90	0.540	0.495	0.485	1.327	1.270	1.073	1.091	1.020	1.007
1.20	2.460	2.800	3.000	2.407	2.036	2.532	2.522	2.600	2.660
1.50	6.100	7.900	9.000	3.416	2.124	3.250	3.260	3.170	3.180
2.00	15.100	22.200	26.800	6.800	2.287	4.090	4.610	6.070	2.960
REDUCED PRESSURE = 1.0									
0.60	0.027	0.016	0.012	0.163	0.271	0.110	0.113	0.089	0.080
0.75	0.163	0.125	0.111	0.436	0.508	0.320	0.327	0.275	0.254
0.90	0.540	0.495	0.485	0.773	0.817	0.699	0.695	0.658	0.654
1.20	2.460	2.800	3.000	1.452	1.220	1.512	1.512	1.550	1.580
1.50	6.100	7.900	9.000	1.979	1.221	1.865	1.871	1.821	1.850
2.00	15.100	22.200	26.800	3.800	1.314	2.260	2.386	1.811	1.613
REDUCED PRESSURE = 2.0									
0.60	0.027	0.016	0.012	0.196	0.493	0.212	0.208	0.211	0.210
0.75	0.163	0.125	0.111	0.422	0.555	0.357	0.359	0.324	0.312
0.90	0.540	0.495	0.485	0.597	0.666	0.566	0.566	0.549	0.551
1.20	2.460	2.800	3.000	1.020	0.846	1.050	1.050	1.068	1.084
1.50	6.100	7.900	9.000	1.321	0.800	1.221	1.224	1.177	1.170
2.00	15.100	22.200	26.800	2.341	0.780	1.390	1.470	1.106	0.985
REDUCED PRESSURE = 5.0									
0.60	0.027	0.016	0.012	0.579	2.840	1.946	1.228	1.696	2.218
0.75	0.163	0.125	0.111	0.750	1.248	0.805	0.795	0.811	0.822
0.90	0.540	0.495	0.485	0.745	0.860	0.747	0.735	0.740	0.751
1.20	2.460	2.800	3.000	0.980	0.793	0.980	0.905	0.982	0.993
1.50	6.100	7.900	9.000	1.101	0.652	0.989	0.996	0.940	0.929
2.00	15.100	22.200	26.800	1.650	0.524	0.933	0.987	0.730	0.645

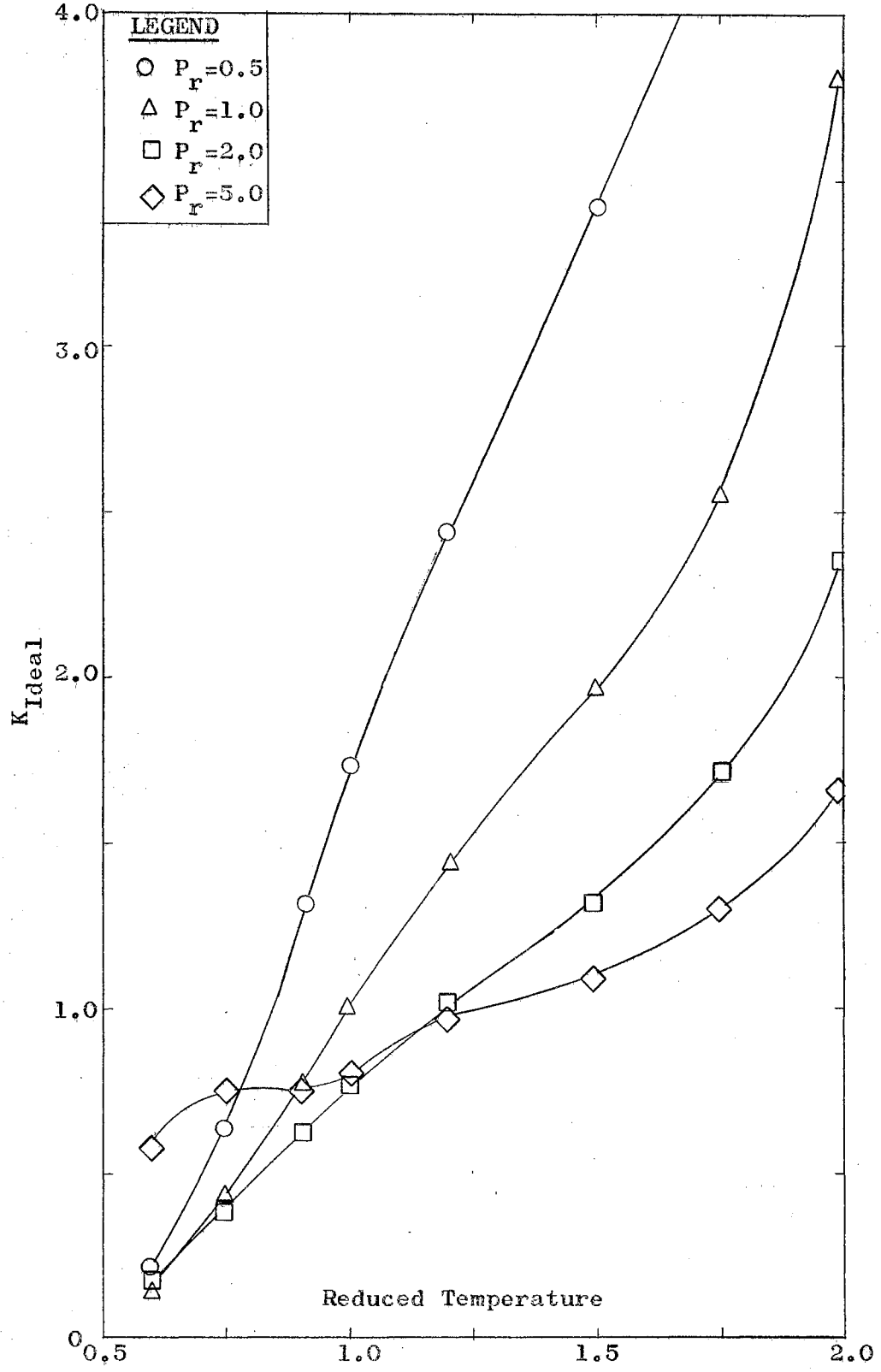

Figure 36

K_{Ideal} for Hydrogen - ω=-0.237

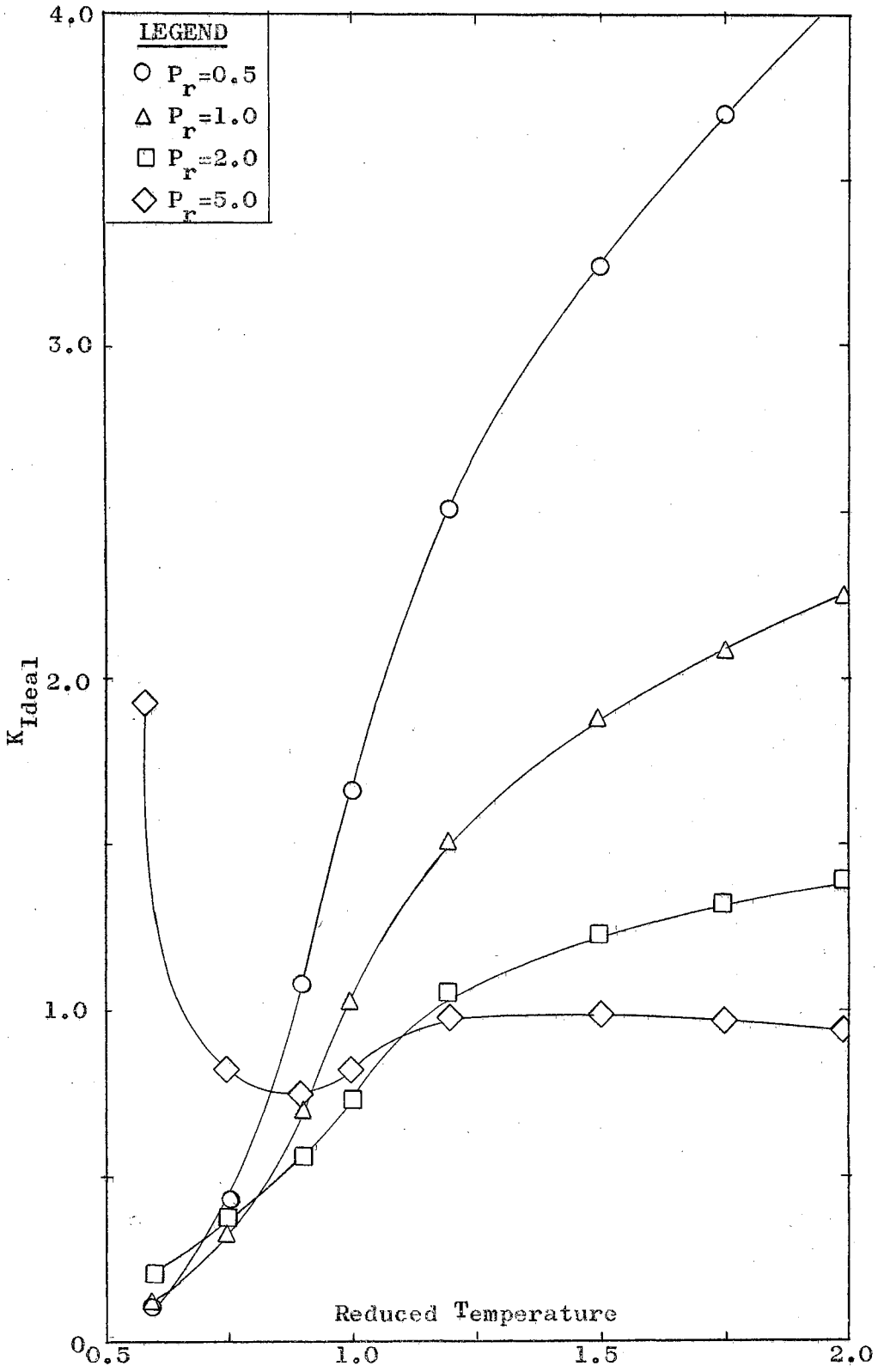

Figure 37

K_{Ideal} for Nitrogen

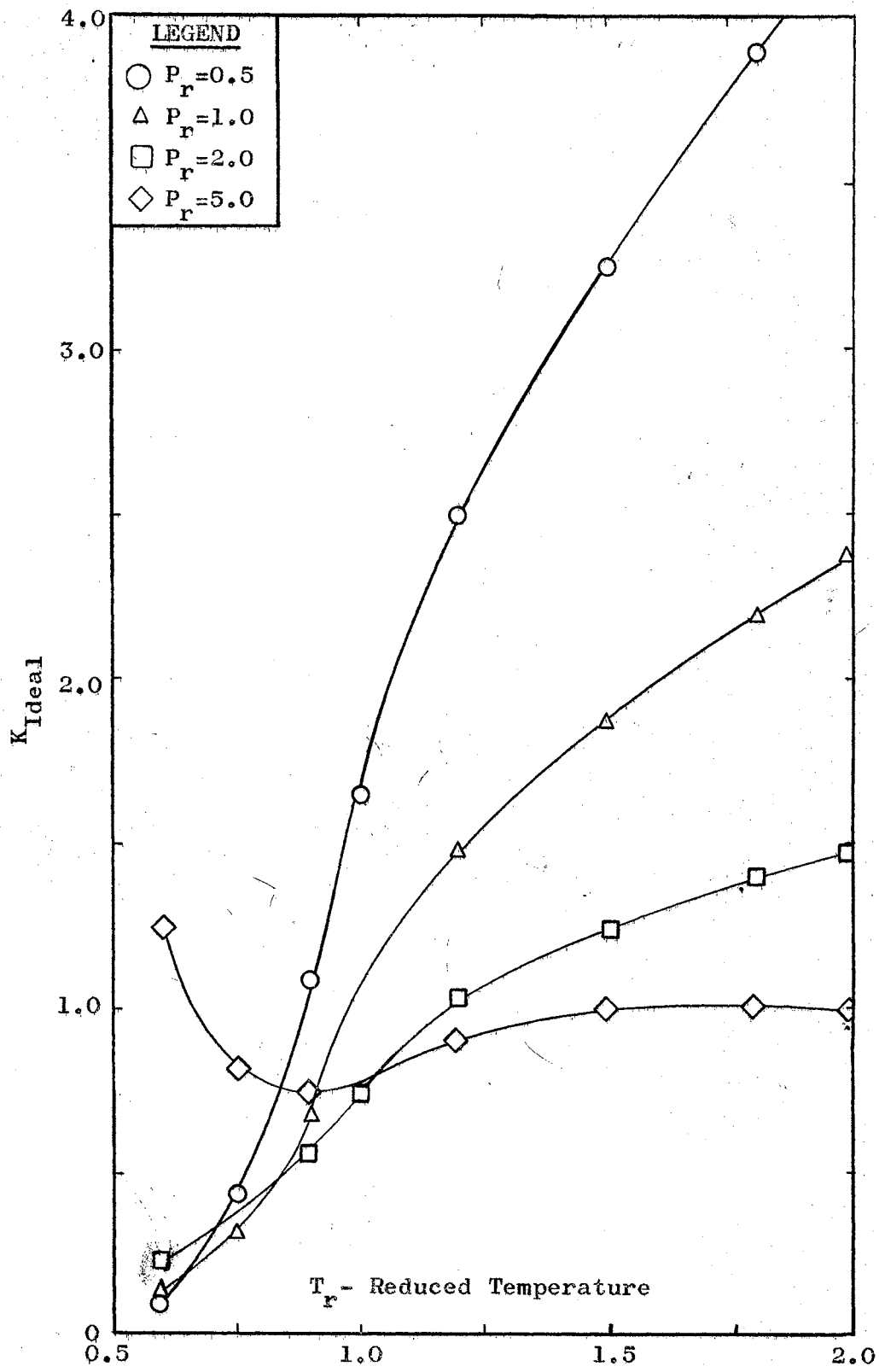

Figure 38

K_{Ideal} for Methane

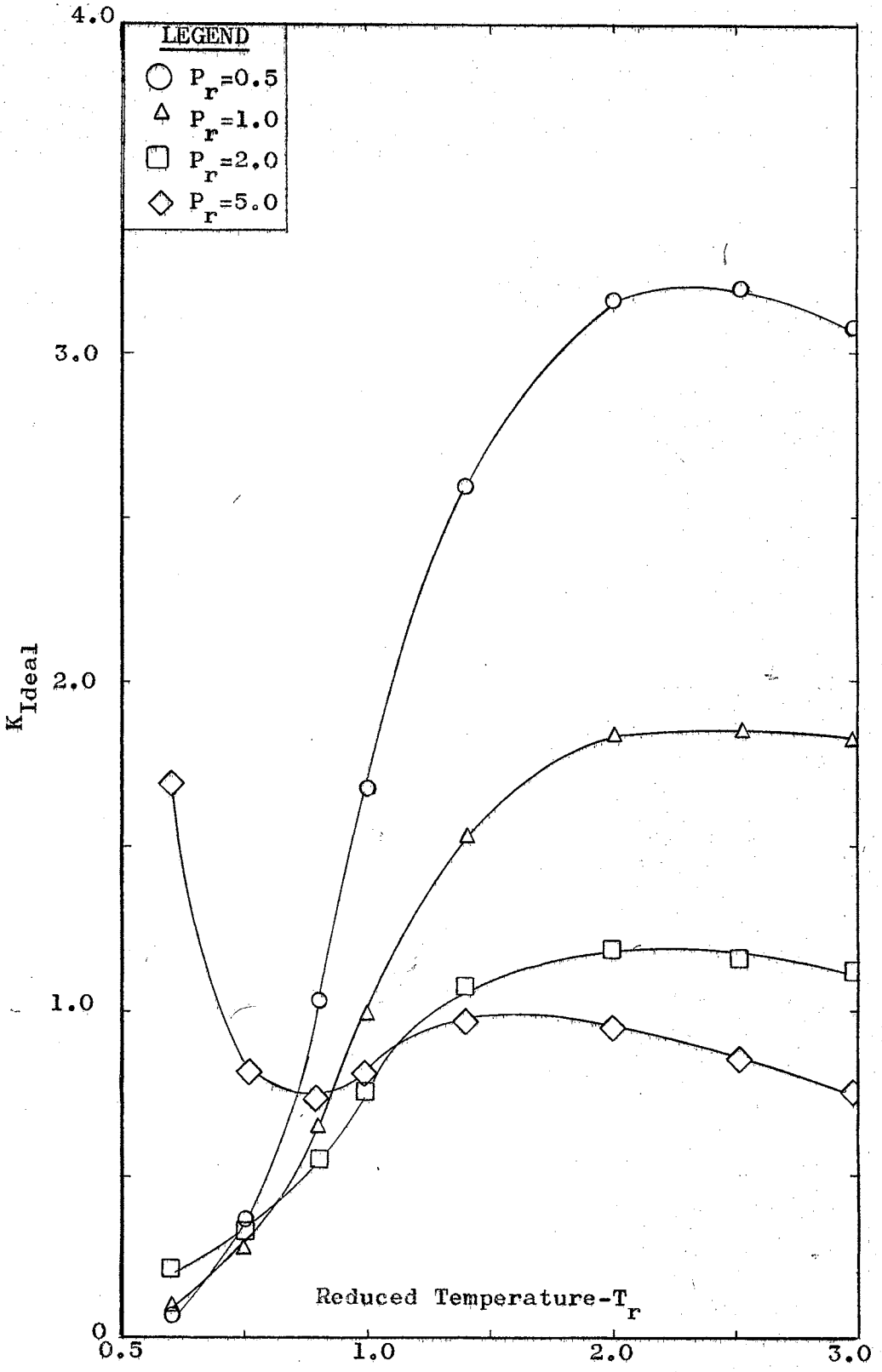

Figure 39

K_{Ideal} for Propane

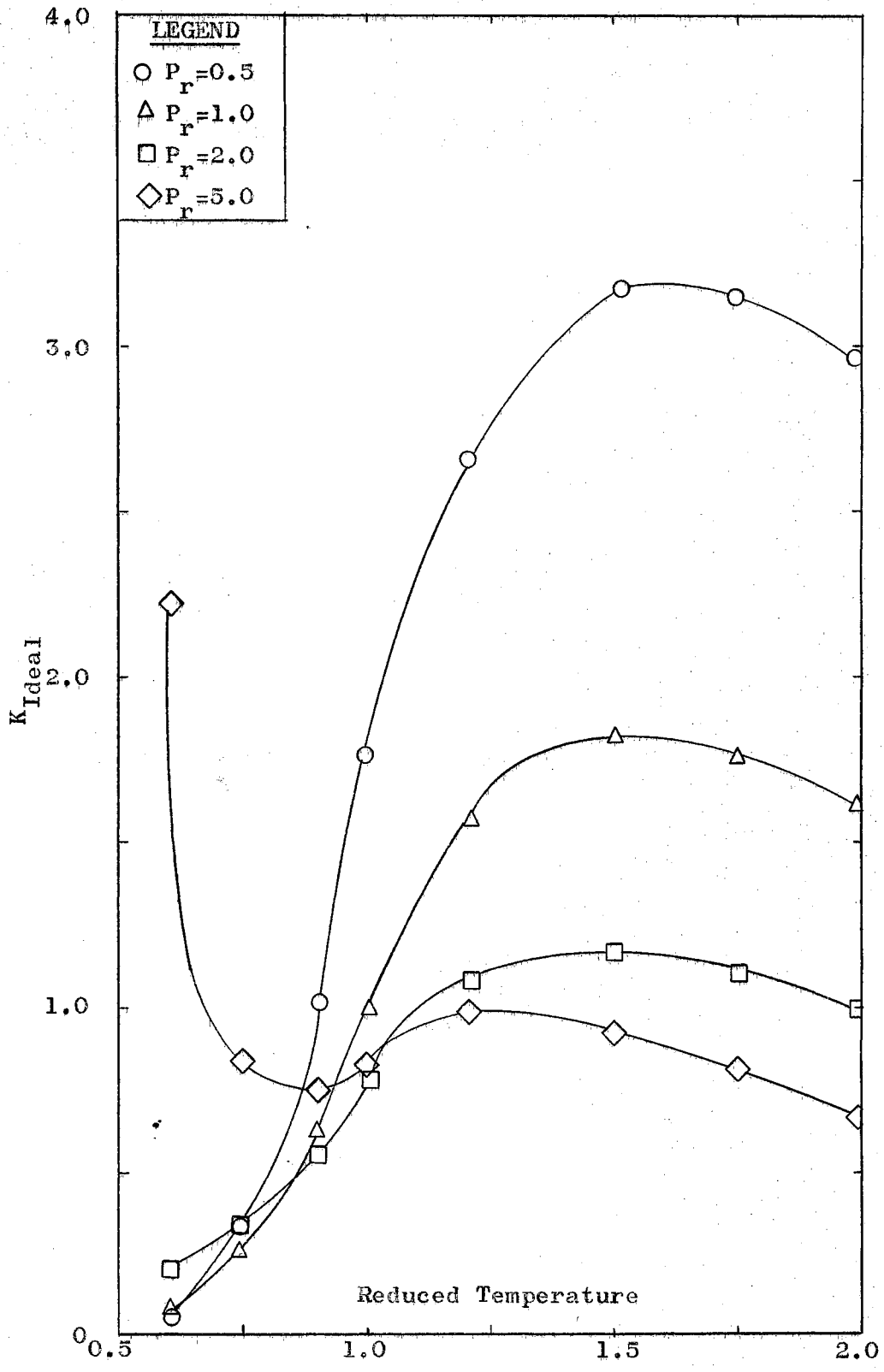

Figure 40

K_{Ideal} for Isopentane

in the early stages of this work. It was suspected that this value was incorrect and that an acentric factor of zero should be used in data correlations. Recent tabulations of calculation constants by Grayson and Streed (32) and Cavett (14) list the acentric factor for hydrogen as zero, giving support to the earlier suspicion about the acentric factor for hydrogen.

K_{Ideal} for hydrogen was reevaluated using the zero acentric factor. Results are plotted as a function of reduced temperature at constant reduced pressure in Figure 41. The change in acentric factor did produce ideal k-values exhibiting a reverse solubility. This is evidence for use of an acentric factor of zero for hydrogen in future calculations.

The ideal K-values for methane went through a maximum at relatively low reduced temperatures. Actual vapor-liquid equilibria data was examined to see if this was reasonable. It was found that methane does exhibit a reverse solubility as do nitrogen and hydrogen. The values of T_r and P_r where the reverse solubility of methane appeared to occur were fairly close to the maximum in the K_{Ideal} curve for methane.

The results of this study indicate that the vapor pressure correlations with the straight line extrapolation at greater than unity reduced temperatures as given in Equation D-2 through D-6 are adequate for this work.

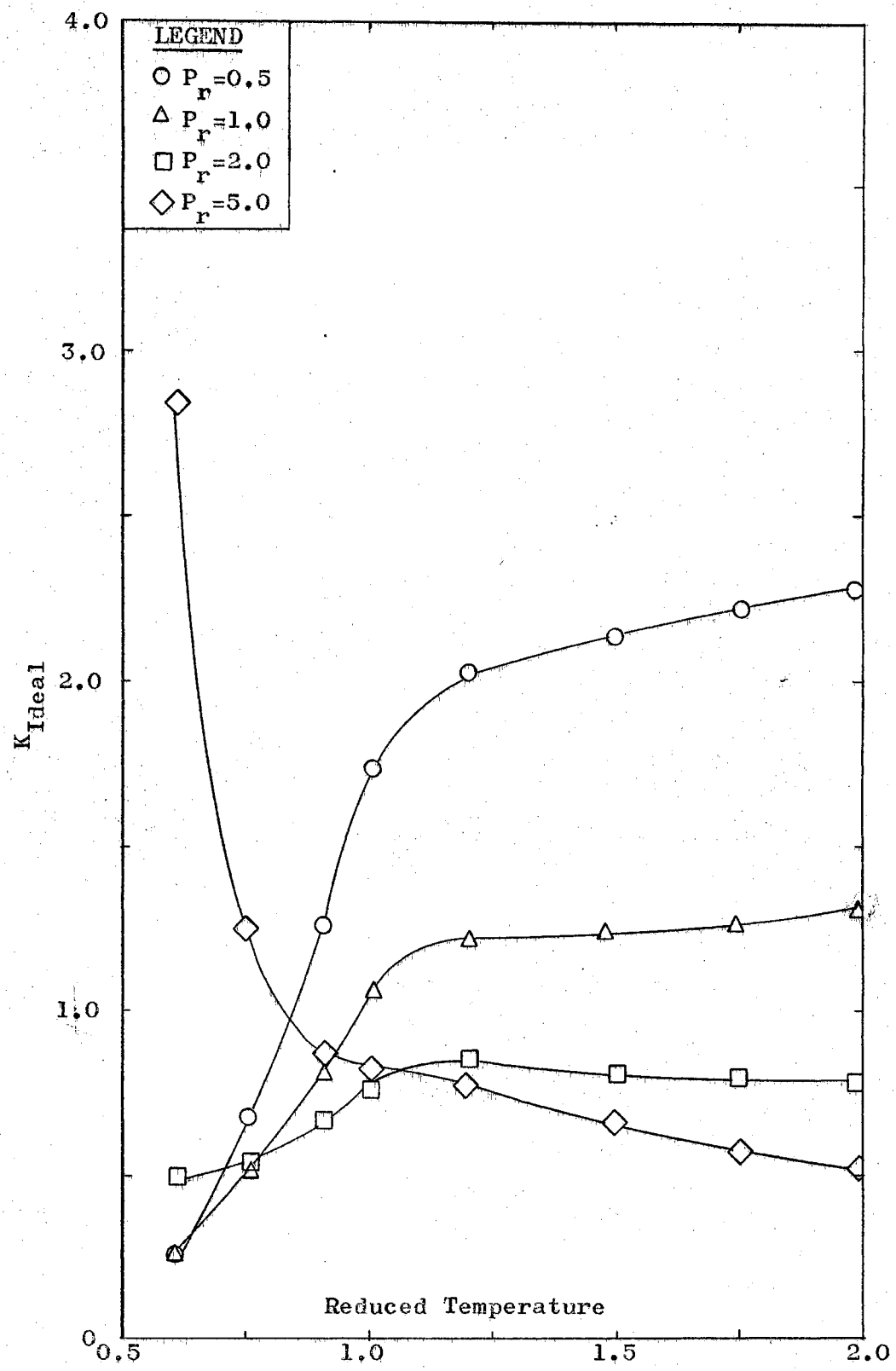

Figure 41

K_{Ideal} for Hydrogen - ω =0.0

APPENDIX E

DEVELOPMENT OF A GENERALIZED EQUATION FOR THE THIRD VIRIAL COEFFICIENT

Values for the third virial coefficient, C, can be found from compressibility factor data and the second virial coefficient, B. A generalized equation for the third virial coefficient was derived using the Pitzer-Curl equation (Equation B-17) for the second virial coefficient and the Pitzer (51) generalized compilations of Z^o and Z'. The procedure used in this development is as follows:

1. At a selected value of reduced temperature and acentric factor, evaluate the second virial coefficient, B, from Equation B-17.
2. Tabulate values of Z^o and Z' at various values of reduced pressure.
3. Calculate Z using Equation B-16 for each value of reduced pressure.
4. Evaluate $\rho = P_r/ZT_r$
5. Calculate $B\rho$
6. Calculate $Z-1-B\rho$
7. Plot $Z-1-B\rho$ vs. ρ^2
8. The slope of this plot = $CP_c^2/(RT_c)^2$
9. Repeat the above steps for other combinations of reduced temperature and acentric factor. The choice of values of reduced temperature is limited by the values of T_r in the Pitzer tabulation.

10. Fit the model

$$C = C^{o} + \omega C' \qquad \text{(E-1)}$$

by plotting C vs. acentric factor for each reduced temperature. Using the least squares criterion, draw the best straight line through the data points. The intercept at zero acentric factor is C^{o}. The slope is C'.

11. Using regression techniques C^{o} and C' were correlated as a function of reduced temperature using the following models

$$\frac{C^{o}(RT_c)^2}{P_c^2} = C_1 + C_3 T_r^{-1} + C_5 T_r^{-2} + C_7 T_r^{-3} \qquad \text{(E-2)}$$

$$\frac{C'(RT_c)^2}{P_c^2} = C_2 + C_4 T_r^{-1} + C_6 T_r^{-2} + C_8 T_r^{-3} \qquad \text{(E-3)}$$

12. Combining Equations E-1, E-2 and E-3, the final equation was obtained

$$\frac{CP_c^2}{(RT_c)^2} = (0.10844 + 0.3895\omega) + (-0.3387 + 1.211\omega)T_r^{-1} + (0.4058 - 1.304\omega)T_r^{-2} + (-0.1358 + 0.478\omega)T_r^{-3} \qquad \text{(B-18)}$$

Equation B-18 is for the Leiden third virial coefficient and is derived with the assumption that the Leiden virial equation of state terminates with the third virial term. Equation V-14 for the imperfection pressure correction requires the Berlin virial coefficients. The relationships between the Leiden and Berlin coefficients are given in Equations V-13a, V-13b and V-13c.

Testing of the Equation

C values from Equation B-18 were compared with values of C

derived directly from PVT data, using the Pitzer-Curl equation (Equation B-17) for the second virial coefficient. Results of this comparison are presented in Table XXV. There is good agreement between the C' (Berlin) values for methane and for propane. The comparison of the C' values for heptane indicates that an improvement in Equation B-18 for C and possibly the Pitzer-Curl equation for the second virial coefficient is needed.

A second test of Equation B-18 was made whereby the quantity $CP_c^2/(RT_c)^2$ was used in obtaining a solution to Equation V-9. This application of Equation B-18 is discussed in Appendix F.

TABLE XXV

COMPARISON OF THIRD VIRIAL COEFFICIENTS DERIVED FROM PVT DATA AND CALCULATED BY EQUATION B-18 FOR THREE HYDROCARBONS

Methane

T_r	B' cc/g mole Pitzer-Curl Equation	C' , cc/g mole atm. From PVT Data (57)	C' , cc/g mole atm. New Equation
0.8	-178.400	-2.041	-2.306
0.9	-138.300	-0.9812	-0.9629
1.0	-115.258	-0.5665	-0.5503
1.1	- 93.500	-0.2910	-0.2810
1.2	- 79.689	-0.1642	-0.1552
1.3	- 66.920	-0.0784	-0.0698

Propane

T_r	B' cc/g mole Pitzer-Curl Equation	C' , cc/g mole atm. From PVT Data (78)	C' , cc/g mole atm. New Equation
0.8	-409.210	-8.4172	-8.5654
0.9	-317.138	-5.0019	-4.9137
1.0	-251.071	-3.0965	-3.0349
1.1	-201.461	-2.0627	-1.9941
1.2	-162.973	-1.4027	-1.3615
1.3	-132.339	-0.9843	-0.9669

n-Heptane

T_r	B' cc/g mole Pitzer-Curl Equation	C' , cc/ g mole atm. From PVT Data (85)	C' , cc/ g mole atm. New Equation
0.8	-1045.50	-25.184	-26.168
0.9	- 778.21	-10.971	-11.974
1.0	- 593.06	- 5.318	- 5.611
1.1	- 444.26	- 2.181	- 2.348
1.2	- 353.93	- 0.945	- 1.030
1.3	- 273.38	- 0.186	- 0.269

APPENDIX F

SOLUTIONS TO EQUATION V-9

The following general relationship for the imperfection pressure correction was derived and presented in Chapter V

$$\ln \Theta_i = \frac{1}{RT}\int_{p_i^o}^{P} (V_i^V - \frac{RT}{P})\, dP - \frac{1}{RT}\int_{p_i^o}^{P} V_i^L\, dP \qquad (F\text{-}1)$$

Two solutions to Equation F-1 will be presented and discussed. In both of these solutions hypothetical vapor or liquid states are encountered.

Pressure-Series Equation of State Solution

In this solution V_i^L is assumed to be constant between p_i^o and P. V_i^V is evaluated via the Berlin form of the virial equation of state

$$PV_i^V = RT + B_i'P + C_i'P^2 + \ldots\ldots \qquad (F\text{-}2)$$

Substitution of Equation F-2 into Equation F-1 and integrating gives

$$\ln \Theta_i = \frac{1}{RT}\left[(B_i' - V_i^L)(P - p_i^o) + \frac{C_i'}{2}(P^2 - p_i^{o2}) + \ldots\right] \qquad (F\text{-}3)$$

The vapor volume is accounted for in the virial coefficients, B_i', C_i', etc. while the liquid volume, V_i^L, is taken as a constant. Equation F-3 is applied and discussed in detail in Chapter V.

Density Series Equation of State Solution

In this solution the liquid and vapor volumes are replaced by the terms of the Leiden form of the virial equation of state.

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\ldots \qquad \text{(F-4)}$$

The individual terms of Equation F-4 can be written

$$\frac{B}{V} = \frac{BP_c}{RT_c}\,\frac{P_r}{ZT_r} \qquad \text{(F-5)}$$

$$\frac{C}{V^2} = \frac{CP_c^2}{R^2T_c^2}\left(\frac{P_r}{ZT_r}\right)^2 \qquad \text{(F-6)}$$

$$\frac{D}{V^3} = \frac{DP_c^3}{R^3T_c^3}\left(\frac{P_r}{ZT_r}\right)^3 \qquad \text{(F-7)}$$

Substitution of Equations F-4 through F-7 into the first term of Equation F-1 and integrating gives

$$\frac{1}{RT}\int_{p_i^o}^{P}\left(V_i^V - \frac{RT}{P}\right)dP = \frac{2BP_c}{RT_c}\,\frac{1}{T_r}\left[\frac{P_r}{Z^v_{P_r}} - \frac{p_r^o}{Z^{v\,o}_{p_r}}\right]$$

$$+ \frac{3}{2}\,\frac{CP_c^2}{R^2T_c^2}\,\frac{1}{T_r^2}\left[\left(\frac{P_r}{Z^v_{P_r}}\right)^2 - \left(\frac{p_r^o}{Z^{v\,o}_{p_r}}\right)^2\right]$$

$$+ \frac{4}{3}\,\frac{DP_c^3}{R^3T_c^3}\,\frac{1}{T_r^3}\left[\left(\frac{P_r}{Z^v_{P_r}}\right)^3 - \left(\frac{p_r^o}{Z^{v\,o}_{p_r}}\right)^3\right]$$

$$+ \ldots\ldots\ldots\ldots - \ln\frac{Z^V_{P_r}}{Z^{V\,o}_{p_r}} \qquad \text{(F-8)}$$

Equation F-8 is simplified by the substitution of Equation V-17

$$\frac{1}{RT}\int_{p_r^o}^{P_r}\left(V_i^V - \frac{RT}{P}\right)dP = \frac{2b}{T_r}\left[\frac{P_r}{Z^V_{P_r}} - \frac{p_r^o}{Z^V_{p_r^o}}\right]$$

$$+ \frac{3}{2}\frac{c}{T_r^2}\left[\left(\frac{P_r}{Z^V_{P_r}}\right)^2 - \left(\frac{p_r^o}{Z^V_{p_r^o}}\right)^2\right]$$

$$+ \frac{4}{3}\frac{d}{T_r^3}\left[\left(\frac{P_r}{Z^V_{P_r}}\right)^3 - \left(\frac{p_r^o}{Z^V_{p_r^o}}\right)^3\right]$$

$$+ \text{.....} - \ln\frac{Z^V_{P_r}}{Z^V_{p_r^o}} \qquad \text{(F-9)}$$

The second term of Equation F-1 can be obtained by direct integration

$$\frac{1}{RT}\int_{p_r^o}^{P_r} V_i^L\, dP = \frac{V_r^L}{T_r}\left(P_r - p_r^o\right) \qquad \text{(F-10)}$$

The combination of Equations F-9 and F-10 was evaluated for the simple fluid at several pressures with the individual terms being evaluated as follows

1. Two reduced isotherms were selected, namely, T_r=0.90 and T_r=1.10.
2. $Z^V_{P_r}$ and $Z^V_{p_r^o}$ were evaluated by the reduced form of Equation F-4

$$Z = 1 + b\left(\frac{P_r}{ZT_r}\right) + c\left(\frac{P_r}{ZT_r}\right)^2 \qquad \text{(F-11)}$$

3. The reduced vapor pressure was evaluated via Equations D-2 through D-6.

4. The reduced volume was evaluated via Equation C-13.

5. The quantity, b, was evaluated via Equation B-17.

6. The quantity, c, was evaluated via Equation B-18.

7. The ideal K-value was then obtained from Equation V-22.

The results of this evaluation are presented in Figure 42. The ideal K-values for the T_r=1.10 isotherm are reasonable and of the correct form. The ideal K-values for the T_r=0.90 isotherm are reasonable at the lower reduced pressures, but are obviously in error at the higher reduced pressures. An analysis of the values of the individual terms of the combined form of Equation F-9 and F-10 showed that the value obtained for CP_c^2/RT_c^2 is not correct at the lower reduced temperatures. This confirmed a suspicion about the values of this quantity obtained at the lower reduced temperatures and indicates a need for revision of Equation B-18 in this region.

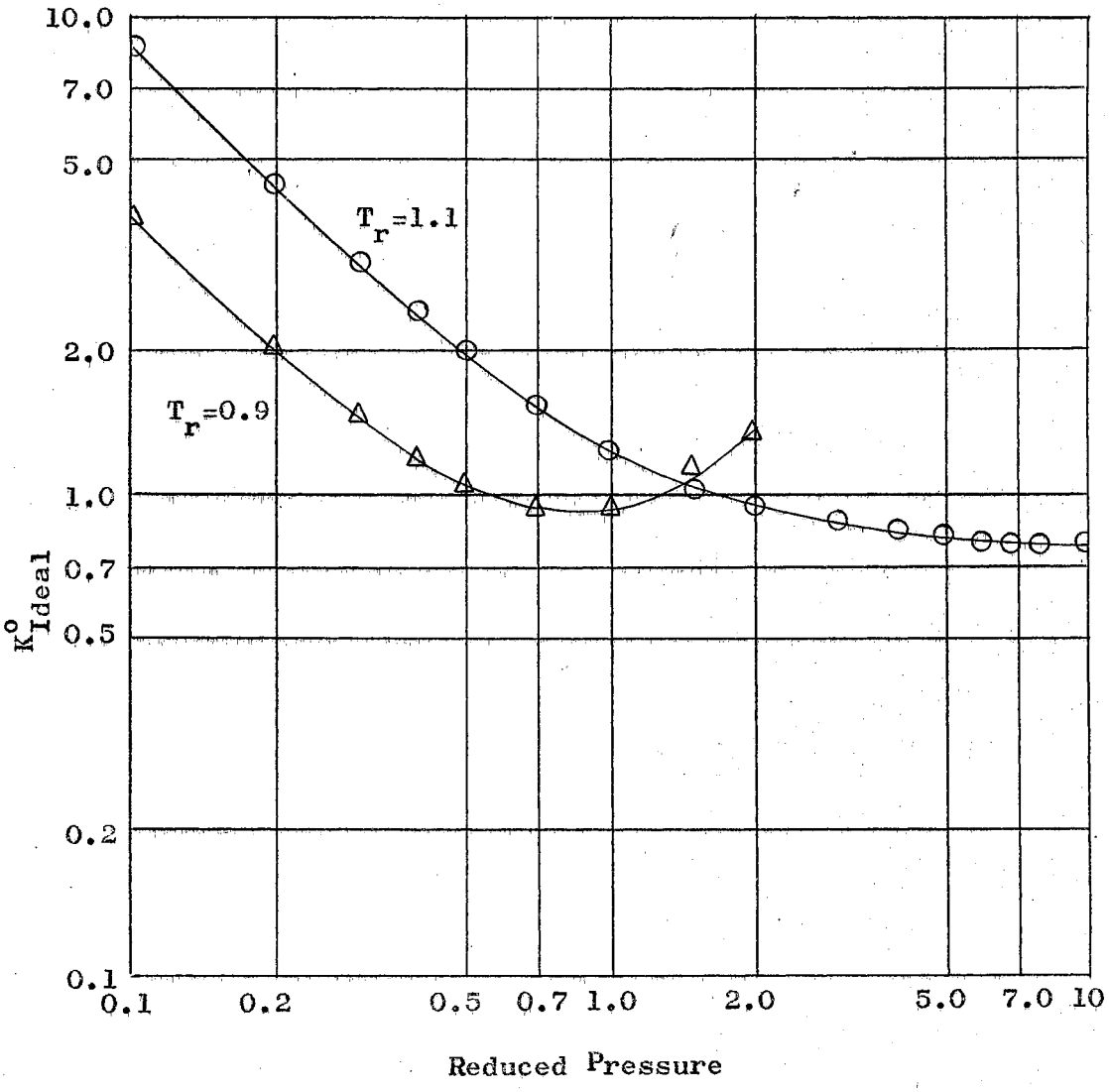

Figure 42

K_{Ideal} via Equation V-9

APPENDIX G

PROCEDURE USED FOR EVALUATING K' FROM GENERALIZED K^o CORRELATION AND VAPOR PRESSURE REQUIREMENT

One method of evaluating the K' correction term is to impose the requirement that $K_{Ideal} = K^o(K')^{\omega} = 1.0$ at the vapor pressure for substances of different acentric factor. Accordingly, the following procedure was used in developing the K' correlation of Figure 7 and in improving the generalized K^o correlation presented in Figure 6. The revised K^o correlation is presented as the dashed portion of Figure 6.

1. Even values of ω from 0 to 0.5 at 0.1 intervals were selected.
2. Even values of T_r over the range of 0.5 to 1.4 were selected.
3. Values of the reduced vapor pressure, p_r^o, were found at each of these T_r and ω values.
4. From the K^o vs. P_r and T_r correlation (Figure 6), values of K^o were found for each point, i.e., each ω value and T_r value.
5. Values of $(K')^{\omega}$ were found as the reciprocal of the K^o value (this follows from the K = 1.0 at the vapor pressure requirement).
6. $(K')^{\omega}$ was plotted against ω for lines of constant T_r and smoothed.
7. From this smoothed plot values of $(K')^{\omega}$ were read. K' was then computed. The average value of K' for each T_r was found.
8. These averaged values of K' were plotted against the

reciprocal of reduced temperature in Figure 7.

9. Using this K' vs. T_r relationship new values of K^o were recomputed for each vapor pressure point (corresponding to each ω) for each reduced temperature.

A sample calculation now follows

1. Given T_r=0.8 and ω=0.1, find K' and K^o revised.

2. From the reduced vapor pressure plot or Equations D-2 through D-6

$$p^o_{r_i} = 0.23$$

3. From the K^o plot, Figure 6, K^o = 1.10

4. $(K')^{\omega} = 1/1.10 = 0.909$

5. The smoothed value of $(K')^{\omega} = 0.91$ from a plot not included of $(K')^{\omega}$ vs. ω.

6. $$K' = (0.91)^{1/\omega} = 0.389$$

7. The average of this and similar calculations at three other ω values gives

$$K'_{average} = 0.386$$

8. Using this K' value, we now find a revised K^o, as follows

$$K^o_{revised} = \frac{1}{(0.386)^{0.1}} = 1.0997$$

for T_r=0.8 and p^o_r=0.23 (the vapor pressure of an ω=0.1 component at T_r=0.8)

The results of the above calculations are shown in Table XXVI.

TABLE XXVI

DEVELOPMENT OF K' CORRELATION FROM GENERALIZED K^o

CORRELATION-REVISION OF K^o CORRELATION

T_r	ω Acentric Factor	$p^o_{r_i}$ Reduced Vapor Pressure	K^o (Figure 6)	K'	K^o Revised (Figure 8)
0.5	0.1	0.0027	1.68	0.00550	1.67
	0.2	0.0015	2.95	0.00675	2.78
	0.3	0.0010	4.60	0.0062	4.62
	0.4	0.0006	7.70	0.00605	7.69
			Average	0.00612	
0.6	0.1	0.0193	1.38	0.040	1.385
	0.2	0.0135	1.85	0.0459	1.92
	0.3	0.0095	2.65	0.039	2.66
	0.4	0.0066	3.30	0.0508	3.68
			Average	0.0416	
0.7	0.1	0.08	1.19	0.176	1.21
	0.2	0.063	1.45	0.156	1.47
	0.3	0.05	1.80	0.142	1.79
	0.4	0.04	2.25	0.132	2.18
			Average	0.143	
0.8	0.1	0.230	1.10	0.389	1.09
	0.2	0.200	1.21	0.386	1.21
	0.3	0.178	1.32	0.396	1.33
	0.4	0.155	1.48	0.375	1.46
			Average	0.386	
0.9	0.1	0.525	1.05	0.614	1.032
	0.2	0.495	1.07	0.713	1.065
	0.3	0.465	1.12	0.686	1.099
	0.4	0.440	1.17	0.676	1.120
			Average	0.691	

TABLE XXVI (Continued)

DEVELOPMENT OF K' CORRELATION FROM GENERALIZED K^o

CORRELATION-REVISION OF K^o CORRELATION

T_r	ω Acentric Factor	$p^o_{r_i}$ Reduced Vapor Pressure	K^o (Figure 6)	K'	K^o Revised (Figure 8)
1.0	---	1.0	1.0	1.0000	1.00
1.1	0.1	1.70	0.99	1.1046	0.99
	0.2	1.77	0.98	1.1041	0.98
	0.3	1.87	0.97	1.1096	0.97
	0.4	1.97	0.95	1.1218	0.96
			Average	1.1061	
1.2	0.1	2.65	0.98	1.2192	0.98
	0.2	2.90	0.965	1.188	0.96
	0.3	3.16	0.95	1.1859	0.95
	0.4	3.48	0.93	1.1992	0.93
			Average	1.1910	
1.3	0.1	3.87	0.96	1.3182	0.975
	0.2	4.37	0.95	1.2825	0.952
	0.3	4.95	0.93	1.2825	0.928
	0.4	5.62	0.905	1.2766	0.905
			Average	1.2825	
1.4	0.1	5.4	0.98	1.4805	0.969
	0.2	6.28	0.95	1.4199	0.938
	0.3	7.3	0.925	1.3848	0.909
	0.4	8.55	0.91	1.3815	0.879
			Average	1.3954	

APPENDIX H

CALCULATION CONSTANTS FOR PURE COMPONENTS

The calculation constants used in this work are tabulated in Table XXVII. The source of these constants is as follows

Critical Temperature, Normal Boiling Point, Critical Pressure

Critical temperatures, critical pressures and normal boiling points for the hydrocarbons were obtained directly from the API 44 compilation. For non-hydrocarbons, these quantities were obtained from the tabulation of the Manufacturing Chemists' Association.

Acentric Factor

Values of the acentric factor were obtained via Equation B-15. The critical properties and the normal boiling points used in the equation were those of Table XXVII.

Solubility Parameter

When available, values of the solubility parameter were taken directly from the tabulation of Hildebrand and Scott (34).

The solubility parameter for those substances not tabulated by Hildebrand and Scott were estimated from the heats of vapori-

TABLE XXVII

CALCULATION CONSTANTS FOR PURE COMPONENTS

NORMAL PARAFFINS	Critical Temp. °R.	Normal Boiling Point, °R.	Critical Pressure atm.	Acentric Factor ω	Hildebrand Solubility Parameter δ @ 25°C.
Methane	343.91	201.01	45.80	0.013	5.45
Ethane	550.01	332.16	48.30	0.105	5.88
Propane	665.95	415.96	42.01	0.152	6.00
Butane	765.31	490.79	37.47	0.201	6.70
Pentane	845.60	556.62	33.31	0.252	7.05
Hexane	914.20	615.42	29.94	0.290	7.30
Heptane	972.31	668.89	27.00	0.352	7.45
Octane	1024.31	717.91	24.64	0.3992	7.55
Nonane	1073.0	763.16	22.60	0.4439	7.65
Decane	1114.7	805.14	20.70	0.4869	7.75
Undecane	1153.7	844.32	19.20	0.5009	7.79
Dodecane	1187.7	881.02	17.80	0.5394	7.84
Tridecane	1220.7	915.49	17.00	0.5818	7.89
Tetradecane	1250.7	948.06	16.00	0.6165	7.92
Pentadecane	1277.7	978.82	14.97	0.6494	7.96
Hexadecane	1303.0	1007.94	14.02	0.6748	7.99
Heptadecane	1328.0	1035.59	13.00	0.6866	8.03
Octadecane	1349.7	1060.35	11.98	0.6959	8.04
ISOPARAFFINS					
Isobutane	734.65	470.58	36.00	0.1918	6.25
Isopentane	829.80	541.82	32.90	0.2060	6.75
Neopentane	780.77	508.79	31.57	0.1950	6.25
Isohexane	896.6	600.36	29.95	0.2824	7.10
3-methylpentane	907.9	605.60	30.83	0.3678	6.35
2,2,dimethylbutane	880.9	581.22	30.67	0.2041	7.00

TABLE XXVII (Continued)

CALCULATION CONSTANTS FOR PURE COMPONENTS

AROMATICS	Critical Temp. °R.	Normal Boiling Point, °R.	Critical Pressure atm.	Acentric Factor ω	Hildebrand Solubility Parameter δ @ 25° C.
Benzene	1012.7	635.87	48.60	0.215	9.15
Toluene	1069.2	690.81	40.15	0.252	8.90
o-xylene	1138.0	751.66	36.06	0.298	8.99
m-xylene	1114.6	742.11	34.70	0.316	8.82
p-xylene	1112.8	740.75	34.02	0.307	8.77
Ethylbenzene	1115.8	738.65	36.74	0.317	8.79
Styrene	1165.7	752.91	39.47	0.248	9.30
OLEFINS					
Propene	657.2	405.83	45.40	0.143	6.43
Ethene	509.51	305.01	50.50	0.0887	6.08
1-Butene	755.3	480.42	39.70	0.203	6.76
cis-2-Butene	770.0	498.39	41.00	0.2725	7.20
trans-2-Butene	770.0	493.27	41.00	0.2336	7.00
1-Pentene	853.0	545.63	39.90	0.2180	7.06
1-Hexene	920.0	606.08	32.10	0.2463	7.40
MISCELLANEOUS COMPOUNDS					
Ammonia	730.1	431.0	111.3	0.266	2.01
Argon	271.3	157.1	48.0	-0.006	9.96
Carbon Dioxide	547.7	-----	72.8	0.225	7.24
Carbon Monoxide	241.2	131.5	35.0	0.0162	6.30
Ethyl Alcohol	928.9	632.8	63.1	0.649	--

TABLE XXVII (Continued)

CALCULATION CONSTANTS FOR PURE COMPONENTS

MISC. CMPDS. (Cont'd.)	Critical Temp. °R.	Normal Boiling Point, °R.	Critical Pressure atm.	Acentric Factor ω	Hildebrand Solubility Parameter δ @ 25°C.
Helium	9.4	7.6	2.26	-0.354	---
Hydrogen	59.8	36.7	12.8	0.000	0.24
Hydrogen Sulfide	672.5	383.1	88.9	0.106	10.99
Krypton	376.9	215.6	54.2	-0.006	21.35
Methyl Alcohol	923.5	607.9	78.7	0.565	
Nitrogen	227.3	139.3	33.54	0.035	7.60
Oxygen	278.6	162.3	50.14	0.017	6.64
Xenon	521.6	298.8	57.62	-0.013	6.06
CYCLOPARAFFINS					
Cyclopentane	921.2	580.4	44.55	0.205	8.10
Methylcyclopentane	959.0	621.0	37.36	0.235	7.85
Cyclohexane	997.7	637.0	38.17	0.203	8.19
Methylcyclohexane	1030.2	673.4	34.32	0.242	7.83

zation and molal volumes of the API 44 tabulation by the following equation (65)

$$\delta = \left(\frac{\Delta H - RT}{V} \right)^{1/2} \qquad \text{(H-1)}$$

If the heat of vaporization was not tabulated by API 44, it was obtained via the Kistiakowsky equation (65)

$$\frac{\Delta H_V}{T_b} = 7.58 + 4.571 \log T_b, \ ^{o}R, \ (\text{Btu/lb. mole } ^{o}R) \qquad \text{(H-2)}$$

The Kistiakowsky equation evaluates the heat of vaporization at the normal boiling point. The heat of vaporization is corrected to 25°C. by the Watson equation (65)

$$\left(\frac{(\Delta H_V)_{25^{o}C.}}{(\Delta H_V)_{NBP}} \right) = \left(\frac{T_c - 537}{T_c - T_b} \right)^{0.38} \qquad \text{(H-3)}$$

APPENDIX I

LIQUID ACTIVITY COEFFICIENT NOMOGRAPH

The procedure for applying the activity coefficient nomographs of Figures 43 and 44 is as follows

Step 1 - Calculate $(\delta_i - \bar{\delta})$, where: δ_i = solubility parameter for the component in question and $\bar{\delta}$ = the liquid volume averaged solubility parameter for the entire liquid phase (Equation VI-6).

Step 2 - Pass a straight line through temperature and $(\delta_i - \bar{\delta})$, locating the turning point on the sloping line that connects the two scales.

Step 3 - Pass a straight line through V_i^L (the molar liquid volume of the component in question) and the turning point found in Step 2.

Step 4 - Read γ_i^L at the point where the line of Step 3 intersects the liquid activity coefficient scale.

The following is a sample calculation for a binary mixture at -100°F. given the data:

	mole fraction	δ $(cal/cc)^{1/2}$	V_i^L cc/g mole
component 1	0.6	10	200
component 2	0.4	4.5	80

The solution by equation is

$$\bar{\delta} = \frac{\sum x_i V_i \delta_i}{\sum x_i V_i} = \frac{(0.6)(200)(10) + (0.4)(80)(4.5)}{(0.6)(200) + (0.4)(80)}$$

$$= \frac{980}{152} = 8.842$$

$$RT = 1.987 \times \frac{360}{1.8} = 397.4 \text{ g cal/g mole}$$

$$\ln \gamma_1 = \frac{V_1(\delta_1 - \bar{\delta})^2}{RT} = \frac{200(10 - 8.842)^2}{397.4} = 0.6749$$

$$\gamma_1 = 1.964$$

The solution by nomograph is as follows

1. Connect $T = 100^{\circ}F$. and $(\delta_1 - \bar{\delta}) = 1.158$, finding the turning point.
2. Connect $V_1 = 150$ with the turning point and intersect scale at $\gamma = 1.964$

From the above it can be seen that the nomograph gives the same γ_1 values as the equation. It does require a preliminary calculation for the $(\delta - \bar{\delta})$ difference, however. No way has yet been found to handle this graphically.

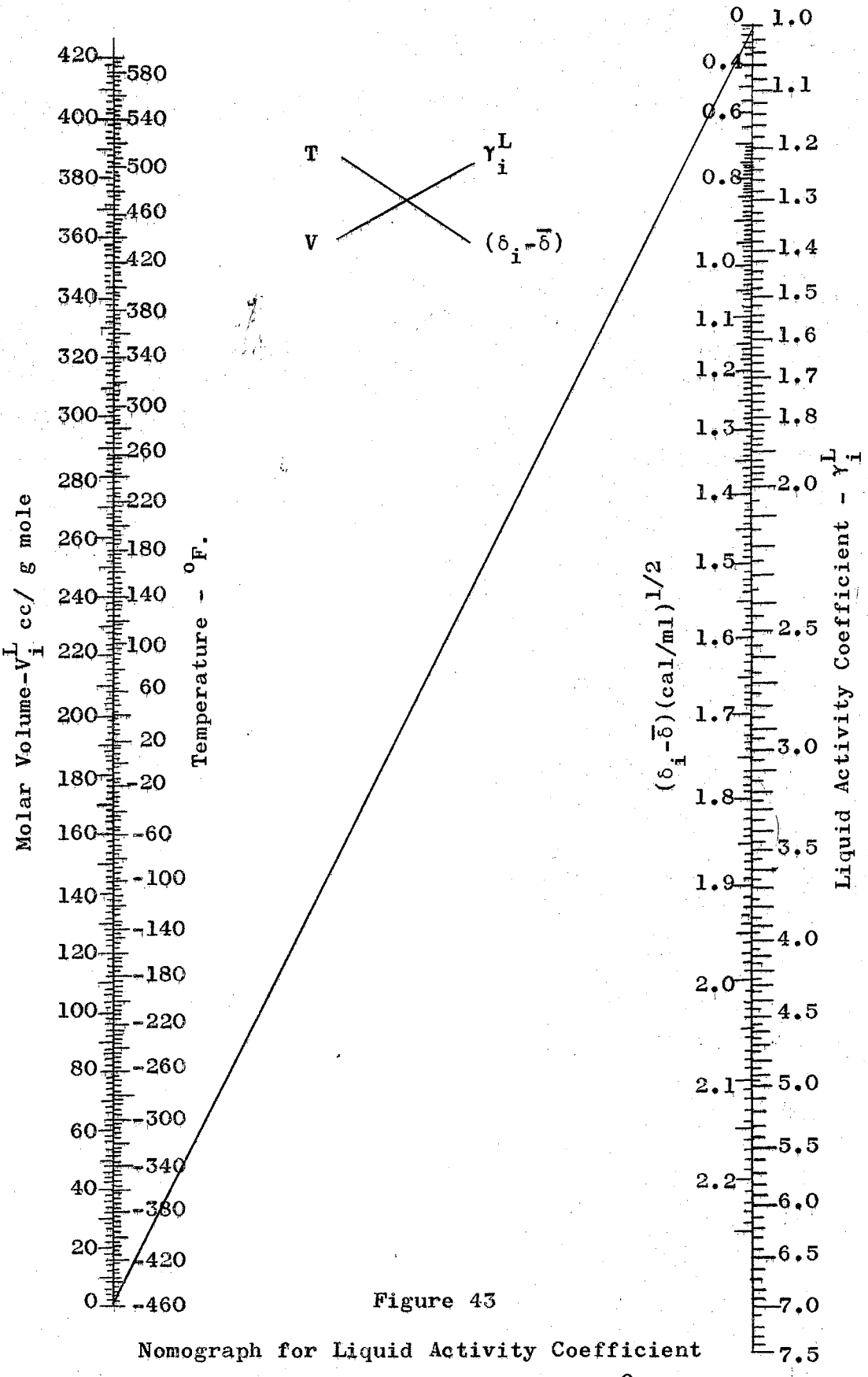

Figure 43

Nomograph for Liquid Activity Coefficient

Temperature Range: -460 to 580°F.

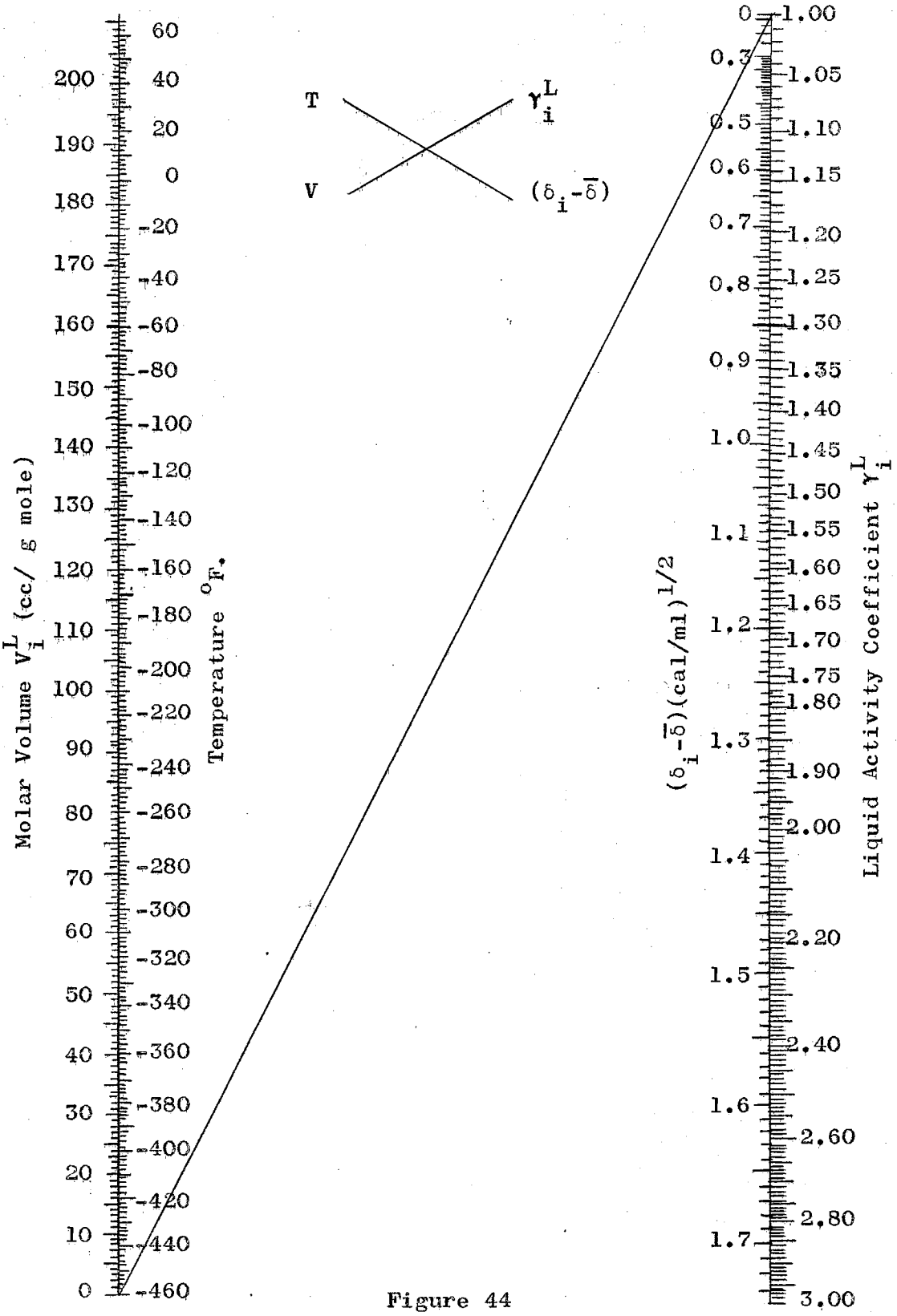

Figure 44

Nomograph for Liquid Activity Coefficient

Temperature Range: -460 to 60°F.

APPENDIX J

SAMPLE CALCULATION FOR HYPOTHETICAL VAPOR FUGACITY COEFFICIENT

The background and equations for the calculation of hypothetical vapor activity coefficients were developed in Chapter IV. A sample calculation now follows. Data is from the 250°F. isotherm of the ethane-n-heptane binary (42).

Step 1 - Calculate ϕ^V_{Ethane} via Equation 35 of Black's paper (10) for each value of T, P, and composition.

Step 2 - Calculate $(f/P)^V_{Ethane}$ for pure ethane via Equation 35 of Black's paper (10) at each T and P.

Step 3 - Calculate γ^V for ethane

$$\gamma^V = \frac{\phi^V_{Ethane}\ (\text{Step 1})}{(f/P)^V_{Ethane}(\text{Step 2})} \qquad \text{(J-1)}$$

A summary of calculations via Steps 1, 2 and 3 is presented in Table XXVIII.

Step 4 - Plot ln γ^V_{Ethane} vs. y_{Ethane} and draw a smooth curve through the data (Figure 11).

Step 5 - Read from the plot made in Step 4 values of ln γ^V_{Ethane} vs. y for even intervals of ln γ^V_{Ethane} and tabulate (Table XXIX).

Step 6 - Integrate the plot of Step 4 numerically using the

trapezoidal rule (Table XXIX),

$$I = \frac{1}{2} \Delta (\ln \gamma^V_{light}) \left[\left(\frac{y_1}{y_2} \right)_1 + 2 \left(\frac{y_1}{y_2} \right)_2 + \left(\frac{y_1}{y_3} \right)_3 \right] = \ln \gamma^V_{heavy} \qquad \text{(J-2)}$$

The subscripts on the brackets in Equation J-2 refer to points on the curve being integrated.

Step 7 - Plot y_{light} vs. $\ln \gamma^V_{heavy}$ and smooth (Figure 11).

Step 8 - Read off $\ln \gamma^V_{heavy}$ at the pressures used in Step 1.

Step 9 - Calculate

$$(f/P)^V_{heptene} = \frac{\phi^V_{heptane} \text{(Eqn. 35 of Black)}}{\gamma^V_{heptane} \text{(Step 6)}} \qquad \text{(J-3)}$$

The calculations of Steps 8 and 9 are summarized in Table XXX.

TABLE XXVIII

CALCULATION OF γ^{V}_{Ethane} IN ETHANE

N-HEPTANE BINARY

P_r	ϕ^{V}_{Ethane} Equation 35 Black (10)	$(f/P)^{V}_{C_2}$	$\gamma^{V}=\frac{\phi^{V}}{(f/P)^{V}}$	y_{C_2}	$\ln \gamma^{V}_{C_2}$
0.0423	1.02178	0.9937	1.0283	0.100	0.0279
0.0479	1.0179	0.9928	1.0253	0.200	0.0250
0.0556	1.01397	0.9917	1.0224	0.300	0.0222
0.0838	1.0032	0.9875	1.0159	0.520	0.0158
0.1043	0.9973	0.9845	1.0130	0.610	0.0129
0.1409	0.9889	0.9791	1.0101	0.705	0.0100
0.2113	0.9760	0.9686	1.0076	0.791	0.0076
0.2818	0.9644	0.9583	1.0064	0.834	0.0064
0.4226	0.9426	0.9376	1.0053	0.878	0.0053
0.5635	0.9216	0.9167	1.0051	0.898	0.0051
0.8453	0.8805	0.8754	1.0058	0.915	0.0058
1.4088	0.7994	0.7903	1.0115	0.916	0.0114

TABLE XXIX

INTEGRATION OF $\ln \gamma^{V}_{Ethane}$ CURVE TO OBTAIN $\ln \gamma^{V}_{Heptane}$-ETHANE-N-HEPTANE BINARY

y_{C_2}	$\ln \gamma^{V}_{C_2}$	y_1/y_2	$\ln \gamma^{V}_{C_7}$
0	0.0307	0	
0.05	0.0293	0.0526	
0.10	0.0279	0.1111	0.00015
0.15	0.0264	0.1765	
0.20	0.0251	0.250	0.00064
0.25	0.0237	0.333	
0.30	0.0222	0.429	0.00231
0.35	0.0208	0.538	
0.40	0.0193	0.667	0.00389
0.45	0.0178	0.818	
0.50	0.0163	1.000	0.00637
0.55	0.0148	1.222	
0.60	0.0132	1.500	0.01021
0.65	0.0117	1.857	
0.70	0.0102	2.333	0.01587
0.75	0.0086	3.000	
0.80	0.0070	4.00	0.02573
0.85	0.0053	5.67	
0.90	0.0036	9.00	0.04642
0.925	0.0027	12.33	
0.95	0.0018	19.00	0.07012

TABLE XXX

CALCULATION OF ν FOR N-HEPTANE IN

ETHANE-N-HEPTANE BINARY

P, psia	P_r	y_{C_2}	$\ln \gamma^V_{C_2}$	$\gamma^V_{C_2}$	y_{C_2}	$\phi^V_{C_2}$	$\gamma^V_{C_2}$
50	0.1260	0.438	0.0046	1.0046	0.562	0.89403	0.88994
100	0.2520	0.705	0.0164	1.0165	0.295	0.82628	0.81287
150	0.3780	0.791	0.0248	1.0251	0.209	0.76492	0.74619
200	0.5040	0.834	0.0310	1.0315	0.166	0.70687	0.68520
300	0.7561	0.878	0.0400	1.0408	0.122	0.59875	0.57528
400	1.0081	0.898	0.0454	1.0464	0.102	0.49458	0.47265
600	1.5121	0.915	0.0583	1.0600	0.085	0.29560	0.27887

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